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STUDIES

FROM THE

PHYSICAL AND CHEMICAL LABORATORIES

OF

THE OWENS COLLEGE.

VOLUME I.

PHYSICS AND PHYSICAL CHEMISTRY.

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PREFACE.

The papers contained in this volume give the results of some investigations carried on in the Physical and in the Chemical Laboratories of the Owens College during the last few years. These investigations were made by members of the teaching staff in conjunction with advanced students, and by Research Fellows of the College, working under the direction of the Professors. One research—that by Mr. J. A. Harker "On the Reaction of Hydrogen with Chlorine and Oxygen"—was begun in the Owens College and finished in the University Laboratory at Tübingen. An account of this work, translated from the *Zeitschrift für Physicalische Chemie*, appears in English here for the first time. The paper by Mr. Haldane Gee and Dr. Harden, "On New Forms of Stereometers," that by Dr. Turpin "On the Duration of Chemical Action in the Explosive Combination of Gases," and several laboratory notes by Dr. Bailey and Mr. Fowler, now appear for the first time. The remaining papers are reprinted from the *Transactions* and *Proceedings of the Royal Society*, the *Journal of the Chemical Society*, the *Memoirs of the Manchester Literary and Philosophical Society*, and the *Philosophical Magazine*.

Owens College,
September, 1893.

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ON THE THERMAL CONDUCTIVITIES OF CRYSTALS AND OTHER BAD CONDUCTORS.

By Charles H. Lees, M.Sc. *(Late Bishop Berkeley Fellow at the Owens College, Manchester).*

(Reprinted from the Phil. Trans. of the Royal Society, 1892.*)*

Introduction.

OUR knowledge of the Thermal Conductivities of Crystals is derived mainly from the experiments of de Senarmont, von Lang, and Jannetaz,* who, using the wax melting or analogous methods, have determined the ratios of what may be called the "principal conductivities" and the positions of the axes of conductivity within a number of crystals belonging to the simple systems. According to their experiments the isothermal surfaces about a heated point in a crystal are, in general, ellipsoids, having their axes parallel to the optical axes. In the case of a uniaxal crystal, this ellipsoid becomes a spheroid of revolution about the axis, and is, as a rule, oblate or prolate according as the wave-surface for the extraordinary ray is oblate or prolate. Although this rule has a number of exceptions, it is sufficiently general to render it probable that there may be some relation between the passage of light and of heat through a crystal. The recent determinations of the refractive indices of metals by Kundt

* Senarmont, *Ann. de Chim. et de Phys.* (3), vols. xxi, xxii, and xxiii (1848); von Lang, *Pogg. Ann.*, vol. cxxxv (1868); Jannetaz, *Ann. de Chim. et de Phys.* (4), vol. xxix (1873)

have shown that they stand in the same order as conductors of heat, and as to the velocity of propagation of light through them, and this fact brings again into prominence the old determinations with respect to crystals. That the comparison which Kundt has made for the metals cannot be carried to other bodies is at once seen from the fact that the index of refraction of iron differs little from those of glass and several commoner crystals, the conductivities of which are shown to be very small compared to that of iron. A comparison may, however, be possible among transparent bodies themselves, and the following experiments were made with the object of furnishing data for this comparison, the results given by previous observers differing greatly from each other. They have, however, been extended to embrace non-transparent bodies commonly in use in a physical laboratory, and about the conductivity of which we have had a very meagre or absolutely no knowledge.

Outline of Method.

The most important consideration in determining the method to be used is the fact that it is difficult to get large pieces of the crystals to be experimented on. This excludes methods requiring large plates, such as that of Weber and Tuschmid, or large spheres or cubes, such as that of Kirchhoff or Thomson. A method which seemed to present several advantages was the one first suggested by Lodge,* and which may be called the "divided bar" method, and after some preliminary experiments had been made to determine its suitability, it was finally adopted. It consists in observing the temperature along a bar heated at one end and cooled at the other, and divided halfway between the two ends by a plane perpendicular to its axis, when (1) the divided ends are together, (2) a disc of the crystal or other body is between.

If temperature observations are taken at several points in each half of the bar, the corrections to be applied to the second set of observations for the distances of the points of observation from the contacts can be determined from the first set, and thus the temperature at each side of the crystal disc can be found. If, in

* *Phil. Mag.* (5), vol. v, p. 110 (1878).

addition, we know the thermal conductivity of the bar used, the amount of heat flowing through the disc can be found from the temperature slope; and thence we have the thermal conductivity of the crystal.

It may be noticed that there would be considerable uncertainty as to the nature of the contacts between bar and crystal unless some special precautions were taken. Lodge proposed to use pads of tinfoil to obviate this difficulty, but this method is not satisfactory. The difficulty has, however, been completely overcome by using bars of a material which would amalgamate, and making the contacts by means of mercury.

Description of Apparatus. (Fig. 1.)

The bar used in the experiments was one of brass, which presents several advantages.

(1) It readily amalgamates, and therefore enables good contacts to be made.

(2) Its conductivity is not so high as to make comparison between it and that of crystals, &c., impossible.

(3) Its conductivity, according to Lorenz, increases with the temperature, a fact which, as will be seen later, partly neutralises the deviation of the cooling from Newton's law.

The diameter of the bar was 1·93 cm., and its length 67 cm. To each end of the bar was soldered a can; through one of these cans steam was sent, and through the other water. The whole was arranged in a wooden frame, so that the bar was horizontal and exposed to the air over a covered tank through which a current of water could be sent to keep the temperature constant. The apparatus was surrounded by paper screens to protect the bar as far as possible from air currents in the room.

The cans at the extremities of the bar were supported on slides attached to the framework in such a way that the bar could be moved parallel to itself by screws passing through the framework and bearing in conical indentations in the backs of the cans in the prolongation of the axis of the bar. These supports were sufficient while the bar was entire, and the experiments to determine its conductivity were being made. After the bar was cut for the insertion of the discs, it became necessary to support the cut ends in such a way as (1) to enable the motion of the bar

parallel to its axis still to take place; (2) to enable the cut faces to be adjusted parallel to each other; (3) to cause as small as possible a disturbance of the isothermal surfaces. These objects were secured by supporting each free end in a loop of thin string,

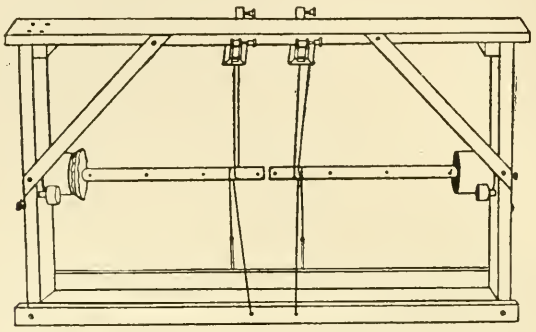

FIG. 1.

hanging from the upper part of the framework. The ends of this loop were attached to screws for the purpose of raising or lowering it as required. The sides of the loop made an angle of 60° or 70° with each other at the bar. These loops were sufficient to support the bars properly if the arrangement was kept horizontal. It was, however, found that the mercury contacts could be made with much greater certainty if the bars were vertical and the mercury surfaces horizontal. On this account two other loops were attached to the lower part of the framework and passed over the bars. These were elastic, and served merely to keep the upper loops taut, and the bars in the same positions with respect to each other, whether the framework was horizontal, as in the experiments, or vertical, as in making the mercury contacts.

MEASUREMENT OF TEMPERATURE.

The most direct method of measuring the temperature along the bar is to sink thermometers into holes in the bar; but this method, although it has been used by Forbes, Tait, and Mitchell for their large bars, is very objectionable, as it diminishes the available area of flow, and therefore makes the change of temperature along the bar more rapid than it would be for a continuous

bar. The method first used by Wiedemann and Franz of measuring the temperature by means of a thermo-junction brought into contact with the bar is free from this objection, and will produce no appreciable effect on the distribution of temperature in the bar if the mass of the junction is not large.

The bars used by Wiedemann and Franz had a silvered surface, and it was sufficient to bring the thermo-couple into contact with the surface in order to get the temperature. In the later of the following experiments the bars were painted, so that contact could not be made in this way. Small conical holes about ·5 mm. deep were, however, made at opposite extremities of horizontal diameters of the bars, and at regular distances along. Eight such diameters were taken, the two nearest the centre of the uncut bar being 1 cm. apart, and the rest 10·5 cms. apart. Each of these small holes was amalgamated, and sufficient mercury left in them to make good contact with the ends of the two wires which were used as a thermo-couple. The thermo-circuit would thus consist at the bars of—first wire of couple; mercury of first hole; brass of bar; mercury of hole at opposite extremity of diameter; second wire of couple. The mercury in the holes was constantly cleaned by touching the surface with dilute nitric acid, washing and drying, and the ends of the thermo-couple wires were kept bright. Under these conditions the arrangement worked satisfactorily.

The wires used originally for the thermo-couple were of brass and iron, but these gave unsatisfactory readings, mainly on account of the poor contact between iron and mercury. As there is an advantage in using copper as one of the elements, a few combinations of copper with other metals and alloys were tried, and eventually the platinum-silver alloy used for resistance coils was selected as the other element. This couple gives an E.M.F. of about ·00016 volt for 70° difference of temperature, and its constant only increases about 7 per cent. for 100° C. It is, therefore, well suited for thermo-electric measurement of temperature. The wires used for the thermo-couple were about 20 cms. long and ·2 mm. diameter. The ends which served to make contact with the galvanometer circuit dipped into mercury cups in blocks of wood which could be moved along guides parallel to the bars in order that the whole of the temperature observations

could be made with one couple. The cup into which the platinum-silver wire dipped was provided with a thermometer graduated in $\frac{1}{10}^{\circ}$ C.

The galvanometer was a low resistance one of the Wiedemann type, with Siemens' bell-magnet and copper damping sphere. The resistance of the whole circuit was only about 1·5 ohm, and as the resistances of the contacts at the holes in the bar might vary, it was necessary to take measurements of the resistance of the circuit when a galvanometer deflection was taken. For this purpose Thomson's modification of the bridge method was used. The diagram (Fig. 2) shows the arrangement of the circuit.

G is the galvanometer in series with the thermo-element. C, D, E are three mercury cups, arranged so that when E and D are connected, the galvanometer and thermo-element are in circuit alone, and when C and D are connected the galvanometer and element form one side of the bridge. K is a reversing switch, and L a key. AB and AF are each 100 ohms from post-office box; FE is a multiple arc box capable of adjustment to $\frac{1}{500}$ ohm. The resistance R of the galvanometer circuit is found by adjusting FE so that there is no effect on the galvanometer on pressing down L, first with K in one direction and then in the other. The coil M is introduced in the battery circuit to counteract the effect of

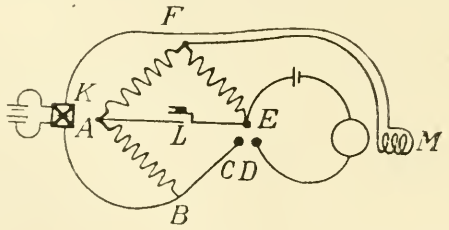

Fig. 2

the current through the galvanometer while making these observations. It will be noticed that the current in it is reversed by the operation which reverses the current in the galvanometer coils, and that the galvanometer needle is therefore kept close to the zero of the scale during the whole of the observations.

Let the values of the resistance EF determined as above be R_1 and R_2, and let P be the resistance of each of the arms AF, AB, W that of the coil M, E the E.M.F. of the battery, e that of

the thermo-element. Then writing down the condition that A and E have the same potential in each case, we have

$$(E + e)\frac{1}{P + R + 2W} = \frac{E}{P + R_1 + 2W}$$

$$(E - e)\frac{1}{P + R + 2W} = \frac{E}{P + R_2 + 2W}.$$

Hence

$$\frac{2}{P + R + 2W} = \frac{1}{P + R_1 + 2W} + \frac{1}{P + R_2 + 2W},$$

which gives

$$R = \frac{R_1 + R_2}{2} - \frac{\{\frac{1}{2}(R_1 - R_2)\}^2}{P + \frac{1}{2}(R_1 + R_2) + 2W}.$$

The last term of the right member of this equation never exceeds $\frac{1}{500}$, and may therefore be neglected, and we have $R = \frac{1}{2}(R_1 + R_2)$.

The constants of the thermo-couple were determined by comparison with a thermometer reading to $\frac{1}{50}$ degree Centigrade. An auxiliary iron bar of 80 cms. length and 2·5 cms. square cross-section, was placed horizontal and heated at one end and cooled at the other by the waste steam and water respectively from the principal bar. The upper surface of this auxiliary bar was tinned and amalgamated. On this surface two copper mercury cups of 1 cm. diameter and 1·8 cm. height were placed. The under surfaces of these cups were amalgamated so as to make good contact with the iron bar. The insides of the cups were amalgamated, and each cup contained sufficient mercury to fill it entirely when the thermometer was placed in it. At opposite extremities of a diameter, about half way down each cup, two small holes like those in the divided bar were punched, and into these holes, which were amalgamated, the wires of the thermo-couple could be inserted. The constants of the couple are in this way determined under exactly the same conditions as when they are in use. The iron bar was buried in sawdust, and the copper mercury cups placed in such positions on the upper surface that the thermometer read in them 90° C. and 55° C. respectively. After the insertion of the wires of the thermo-couple into the holes of the mercury cups, the cups were surrounded with sawdust, and 10 minutes allowed for the temperature of the cups to get as nearly as possible uniform before observations were taken.

In an experiment made in the early part of the work the following observations were taken :—

(*a*) Temperature of hot junction, 85°·90 C.
Temperature of cold junction, 15°·67.
Deflection of galvanometer in scale divisions, 296.
Resistance of circuit, mean of observations taken, as previously described, 1·431 ohm.
E.M.F. of element in units used, 423·6.

(*b*) Temperature of hot junction, 55°·60.
Temperature of cold junction, 15°·74.
Deflection of galvanometer, 162·3.
Resistance of circuit, 1·448 ohm.
E.M.F. of element in units used, 235·0.

These observations are sufficient to determine the constants in the formula $e = a\,(t_2 - t_1)\,(1 + b\,t_2 + t_1)$ where t_2 and t_1 are the temperatures of the hot and cold junctions respectively. It was found more convenient for the reduction of observed E.M.F.'s to temperature, to draw up a small table of values of $a\,(1 + b\,\overline{t_2 + t_1})$ for different values of $t_2 + t_1$. Thus, for the above observations, we have :—

$t_2 + t_1$.	$a(1 + b\,\overline{t_2 + t_1})$.	Differences.	
101° C.	6·030	+ 2° C.	+ ·009
91	5·985	4	·018
81	5·940	6	·027
71	5·895	8	·036
61	5·850		
51	5·805		
41	5·760		
31	5·715		

By inspection we have the divisor for converting E.M.F. observations to temperature difference, since in every case $t_1 + t_2$ is known approximately to within one or two degrees.

The value of $a\,(1 + b\,t_2 + t_1)$ is seen from the above table to change only about 7 per cent. for 100° C. of change of $\overline{t_2 + t_1}$; the platinum-silver-copper element is therefore well suited for thermo-electric observations of temperature.

The determination of the constants of the element was repeated every few days during the progress of the work. The value of a

was found to diminish slowly, the total change during the three months during which the couple was used being about 1·5 per cent.

The temperature of the enclosure in which the divided bar was suspended was determined by means of a thermometer graduated in $\frac{1}{10}$ degrees, placed about 7 cms. above the top of the water tank, and about 15 cms. below the bar. The bulb of the thermometer was protected from radiation from the hot bar by a small sheet of paper, just large enough to screen the bulb.

Determination of the Thermal Conductivity of the Brass Bar.

The thermal conductivity of the bars was determined, following the method of Forbes, by two series of experiments, the first to determine the law connecting the rate of loss of heat from a heated surface, with the temperature of that surface, and the second to determine the law of steady distribution of temperature along a bar heated at one end, and exposed to the air along its entire length. These two observations furnish data for determining the thermal conductivity required.

Cooling Experiments.

It is customary in making these experiments to use a short length of the bar used in the steady experiments. I have, however, shown that the law of cooling is the same for bars of different material, but of the same cross-section and surface; and as a knowledge of the specific heat of the bar is required, it seemed better to make use of a bar of a material the specific heat of which is well known, rather than a brass bar in these experiments. As the values found by different observers for the specific heat of copper are practically identical, this metal was chosen. As it is a better conductor than brass, it also enables the assumption that the temperature throughout the bar is the same to be made without much chance of error. The bar was of the same diameter as the brass bar, 1·93 cm. and 26 cms. long. It had a polished nickel-plated surface. To make the cooling experiment correspond more closely to that of an infinitely long bar, the ends of the bar were covered with a layer of sulphur about 5 mms. thick. This was done by placing the bar vertical, wrapping a sheet of paper

round the upper end, so as to project about 1 cm. above the end, and then pouring melted sulphur into the paper cylinder. Since sulphur is an extremely poor conductor of heat, it may be assumed that the loss of heat from the ends of the bar is very small.

The bar was suspended in the position occupied afterwards by the divided bar by means of threads. The temperature was determined by means of the platinum-silver-copper wires inserted into small holes amalgamated and filled with mercury, on opposite sides of a diameter at the middle of the bar. Observations of current, resistance, temperature of the cool junction, and of the enclosure, were made every two minutes during the experiments. From these observations the temperature of the bar at any time is determined, and curves drawn for each experiment showing the connection between time and temperature of bar and of enclosure. Of these curves that which corresponded most nearly with the mean of all was selected, and is referred to in what follows.

If m is the mass of the bar, s its surface, c the specific heat of the material of the bar, v the excess of the temperature of the bar over that of the enclosure, which will be supposed constant, we have, as the connection between v and time,

$$mc \frac{dv}{dt} + sh_v v = 0 \quad . \quad . \quad . \quad . \quad . \quad (1°)$$

where h_v is a quantity which is generally assumed to be constant (Newton's law), but which I have shown increases for a nickel-plated bar of the size used 70 or 80 per cent. for 100° C. rise of v.* In the paper referred to this rise is expressed by writing $h_v = hv^n$ where n is a small fraction $= \frac{1}{7}$ about. In that paper v was always positive. As in the following work v is sometimes negative, in which case v^n would require special interpretation, it is preferable to write $h_v = h(1 + bv)$ where b is a small positive quantity. The foregoing equation becomes, then,

$$mc \frac{dv}{dt} + sh(1 + bv)v = 0 \quad . \quad . \quad . \quad (2°)$$

the solution of which is

$$\frac{1}{v} + b = Ae^{(sh/cm)t} \quad . \quad . \quad . \quad . \quad . \quad (3°)$$

where A is an arbitrary constant.

---

* *Phil. Mag.*, vol. xxviii, p. 429 (1889).

The following table shows that this equation represents the cooling with a fair amount of accuracy for $b = \cdot 008$. The temperature of the enclosure has been assumed constant = 15°·2 C., but in reality it varied from 15°·3 at the commencement to 15°·4 at $t = 10$ minutes, and then down to 15°·2 at 40 minutes, 15°·18 at 60 minutes, 15°·1 at 70 minutes. On this account no attempt has been made to determine b with greater accuracy; the value given above is determined by trial.

Cooling of Nickel-plated Bar.

t in minutes.	Temperature. − 15°·2 C. = v.	$1/v$.	$\frac{1/v_t + b}{1/v_{t+2} + b} = e^{-(sh/cm)\,120}$	Means.
0	75·4	·01326	..	
2	69·2	1445	·9469	
4	64·03	1562	504	·9468
6	58·67	1704	434	
8	54·36	1840	485	
10	50·14	1994	448	
12	46·58	2147	482	
14	43·30	2309	479	
16	40·16	2490	450	·9467
18	37·37	2676	466	
20	34·80	2874	460	
22	32·43	3084	459	
24	30·31	3299	475	
26	28·28	3536	454	·9462
28	26·43	3784	459	
30	24·72	4045	463	
32	23·16	4318	467	
34	21·77	4593	490	
36	20·44	4892	474	·9466
38	19·10	5236	430	
40	17·95	5576	467	
43	16·22	6165	428	
46	14·95	6689	528	
49	13·67	7315	479	·9474
52	12·49	8006	470	
55	11·41	·08764	465	
60	9·88	·1013		
65	8·51	1175	·9454	·9454
70	7·21	1387		
75	6·26	1597		

The mean of the values of $e^{-(sh/cm)\,120}$ is ·9466.

Hence we have

$$e^{120\,(sh/cm)} = \frac{1}{\cdot 9466} = 1\cdot 0564.$$

Therefore

$$\frac{sh}{cm} = \frac{\cdot 02383}{\cdot 4343} \times \frac{1}{120} = \cdot 0004572.$$

Now, $m = 676$ grms., $s = 157{\cdot}6$ sq. cms., $c = \cdot 093$.

Hence we have $h = \cdot 0001804$.

The heat lost from a nickel-plated surface exposed to air is, therefore,

$\cdot 0001804v\ (1 + \cdot 008v)$ gram degrees per sq. cm. per second, where v is the excess of temperature of the surface over that of the air.

Statical Experiments.

These experiments were made with the brass bar before it was cut. One end was heated by steam, and the other cooled by water. Eight observations of temperature were taken at different points of the bar in the way previously described.

Let v be the excess of temperature at point x of bar over that of surrounding air,

p = perimeter of cross-section of bar,

q = area of cross-section of bar,

k_v = thermal conductivity at temperature excess = v.

Then, at any point of the surface of the bar, we have

$$k_v \frac{dv}{dn} + hv\ (1 + bv) = 0,$$

where dv/dn is the rate of change of v along the normal to the surface, s, h, and b having the meanings assigned to them in last section.

At $v = 60°$ C. this gives

$$k_v \frac{dv}{dn} = - \cdot 00018 \times 60 \times 1{\cdot}5$$
$$= - \cdot 0162.$$

Now k_v will be seen later to have the value $\cdot 27$ approximately. Hence, at a point of surface, at the temperature of 60° C. excess, $dv/dn = - \cdot 06$.

At the same point on the surface $dv/dx = 2{\cdot}5$ approximately. Hence, the inclination of the normal to the isothermal surface at this point to the axis of the bar is arctan $\cdot 06/2{\cdot}5$ = arctan $\cdot 024 = 1° 25'$. If the isothermal surface be assumed to be part of a sphere, the radius of curvature is about 42 cms. At 15° C. excess, a similar calculation gives the radius of curvature of the isothermal surface to be 60 cms.

Hence we may assume the isothermal surfaces to be planes perpendicular to the axis of the bar.

The equation for the motion of heat in the bar is under these conditions

$$q\frac{d}{dx}\left(k_r\frac{dv}{dx}\right) = phv\,(1 + bv). \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The conductivity k_r has generally been considered constant in treating this equation, but this is scarcely justifiable, as most experimenters find changes of $\pm$ 20 per cent. in conductivity for 100° C. change of temperature. Taking therefore k_r as equal to k $(1 + av)$ the above equation becomes

$$(1 + av)\frac{d^2v}{dx^2} + a\left(\frac{dv}{dx}\right)^2 = \frac{ph}{qk}\,v\,(1 + bv). \quad . \quad . \quad . \quad (5)$$

Multiplying through by $2\,(1 + av)\,(dv/dx)$, this becomes

$$2\,(1 + av)^2\frac{d^2v}{dx^2}\frac{dv}{dx} + 2a\,(1 + av)\left(\frac{dv}{dx}\right)^2\frac{dv}{dx}$$

$$= 2\frac{ph}{qk}\,v\,(1 + bv)\,(1 + av)\frac{dv}{dx},$$

or,
$$\frac{d}{dv}\left(\overline{1 + av}\,\frac{dv}{dx}\right)^2 = 2\frac{ph}{qk}\,(v + \overline{a + b}\,v^2 + abv^3)\frac{dv}{dx}.$$

From which by integration we obtain

$$\left(\overline{1 + av}\,\frac{dv}{dx}\right)^2 = \frac{ph}{qk}\left(v^2 + 2\,\frac{a + b}{3}\,v^3 + \frac{ab}{2}\,v^4\right) + \text{constant}.$$

If the value of dv/dx when $v = 0$ be dv_0/dx, the above equation becomes

$$\left(\overline{1 + av}\,\frac{dv}{dx}\right)^2 - \left(\frac{dv_0}{dx}\right)^2 = \frac{ph}{qk}\,v^2\left(1 + 2\,\frac{a + b}{3}\,v + \frac{ab}{2}\,v^2\right). \quad . \quad . \quad (6)$$

If $dv_0/dx = 0$, the integral of this equation can be expressed in terms of logarithmic and circular functions. If $dv_0/dx = 0$, the integration introduces circular functions and elliptic integrals of the 1st and 3rd kind. If the problem under discussion were—given the conductivities—to determine the distribution of temperature throughout the bar, this integration would be necessary; but as we are given the distribution and have to find the conductivity, the problem can be solved without further integration. Although this method is probably not as accurate as that depending on the integrated equation, its accuracy is sufficient for the present purpose, where the value of the conductivity is only required over a small range (25° 37° C.) of temperature.

To determine dv/dx at the points of observation v is represented by an empirical function of x, and the differential co-efficient with respect to x taken. The known conditions which v satisfies, fix, to some extent, the function to be used; we see, *e.g.*, that it vanishes for some value of x, and that at that point the first differential co-efficient is finite; that it increases in one direction with x in an approximately exponential manner. These considerations lead at once to the function A sinh $(Ax + \beta)$, and this function has been used. It evidently cannot express v accurately throughout the bar, since it is the solution of a linear differential equation, but it can be made by a proper choice of the constants to represent the main feature of the curve, the differences between its values and those observed being afterwards represented by an additional expression, which has generally only small values.

For the curve which corresponded best with the mean of the three sets of observations taken, the value of v is represented along the cooler part of the bar by ·795 cosh ·0378 x + 11·86 sinh ·0378 x.

x	v calculated.	v observed.	Difference.	$\frac{dv}{dx}$.
0	·8	·8	0	·448
10·56	5·72	5·72	0	·497
21·04	11·52	11·53	+ ·01	·624
31·55	19·17	19·18	+ ·01	·852
32·59	20·07	20·09	+ ·02	·881
43·15	31·23	31·20	− ·03	1·262
53·59	47·24	47·88	+ ·64	1·971
64·03	70·64	73·47	+2·83	3·002

The differences, with the exception of the last two, are within the limits of error of observation, and may be neglected. The last two may be taken into account by adding to the above expression for v, between $x = 43$ and $x = 64$, an expression of the form

$$a\left(\frac{x - 43}{10{\cdot}5}\right)^2 + b\left(\frac{x - 43}{10{\cdot}5}\right)^3, \text{ where } a = {\cdot}572,\ b = {\cdot}067.$$

The values of the differential co-efficient of this expression at $x = 43{\cdot}15$, $53{\cdot}59$, $64{\cdot}03$ are 0, ·128, ·294 respectively. Differentiating the hyperbolic expression for v we have dv/dx = ·03005 sinh ·0378 x + ·4483 cosh ·0378 x, which gives, on substituting for x the co-ordinates of the points of observation, the required values of dv/dx, to which, at $x = 53{\cdot}59$ and $64{\cdot}03$, we

must add the quantities ·128 and ·294 to get the true temperature slope. The values thus obtained are given in the above table.

Having thus got the values of v and dv/dx at eight points on the bar, we can by trial determine a so that the equation (6) holds. A few trials show that a is positive and equal approximately to ·002. It is not necessary to determine a with any great accuracy, as it affects very little the subsequent work. Assuming $a = ·002$ we have the following table of results:—

x.	v.	$v^2\left(1 + 2\frac{a+b}{3}v + \frac{ab}{2}v^2\right)$	$\left(1 + av\frac{dv}{dx}\right)^2$	(5)	(6)
0	·8	·643	·201	·001	·0016
10·56	5·72	33·96	·253	·053	·0015
21·04	11·53	143·3	·406	·206	·00143
31·55	19·18	415	·781	·581	·00140
32·59	20·09	459	·839	·639	·00139
43·15	31·20	1174	1·796	1·596	·00136
53·59	47·80	3067	4·666	4·466	·00145
64·03	73·47	8269	11·860	11·660	·00141

Column (5) gives the values of $\left(1 + av\frac{dv}{dx}\right)^2 - \left(\frac{dv}{dx}\right)^2$, and column (6) gives the values of

$$\frac{\left(1 + av\frac{dv}{dx}\right)^2 - \left(\frac{dv}{dx}\right)^2}{v^2\left(1 + 2\frac{a+b}{3}v + v^2\right)},$$

which by equation (6) $= ph/qk$.

Neglecting the first two numbers in column (6), which are uncertain on account of the smallness of the quantity (5) at the cool end of the bar, we have, as the mean value of ph/qk, ·00141.

Hence

$$k = \frac{ph}{·00141\,q} = \frac{2·093 \times ·0001804}{·00141} = \frac{·0003777}{·00141} = ·268 \frac{\text{gram.}}{\text{cm. sec.}}$$

The temperature of the air in this experiment was 17° C., hence we have for the thermal conductivity of the brass bar used

$$k = ·268\,(1 + ·002\,v - 17) \frac{\text{gram.}}{\text{cm. sec.}}.$$

* The following values of k for brass have been found by different experimenters: Neumann, *Ann. de Chim. et de Phys* (3), vol. lxvi (1862), ·302; Weber, *Monatsber. Berlin Akad.* for 1880, p. 457. 150; Lorenz, *Wied. Ann.*, vol. xiii (1881); "red brass," ·252 (1 + ·0018 t.); "yellow brass," ·212 (1 + ·0020 t.).

Experiments on Crystals, &c.

Before cutting the bar for the insertion of the discs the conductivities of which were to be measured, several observations were made of the distribution of temperature along the bar after it had been painted with Aspinall's enamel. It is necessary to have the radiating surfaces of bar and discs the same, and this is most easily secured by painting both. The loss of heat from a point of the surface at any temperature is about 40 per cent. greater than the loss at the same temperature for the nickel-plated surface, but it does not increase as rapidly with rise of temperature. On this account it is possible to express the distribution of temperature along the bar in the empirical form $v = A \sinh(\alpha x + \beta)$, and A, α, and β can be determined so that this equation holds with a closer approximation than in the case of the unpainted bar, throughout the whole length of the bar. It is assumed to hold in what follows for each half of the divided bar, α having the same, but A, β having different values for each half.

The bar was divided in the middle, between the contact holes 1 cm. apart, and the ends ground down to be as nearly as possible planes perpendicular to the axis of the bar. To secure this a vertical hole, a little larger than the bar, was drilled in a prism of wood, 30 cms. $\times$ 20 cms. base, and 15 cms. height. This was done in a drilling machine, the table of which was found to be perpendicular to the spindle. One of the bars was then fixed by wedges into this hole in such a way that a point, which when the bar was in position would be the highest point of the cut surface, came in contact with a mark on the block of wood. The block and bar were then moved about on a stone and afterwards on a slate slab, till the surface was plane and smooth. The other bar was then fixed so that the lowest point of the cut surface came into contact with the same mark, and the surface rubbed down. This process secured that the cut surfaces should be parallel to each other when the bars were co-axal. To secure and test that the surfaces were parallel when the bars were in position in the framework, two test gauges were made, one for testing the upper surface and the other the side of the bars. The bars were taken out of the frame and placed vertical, the upper bar resting with its cut surface accurately on the cut surface of the lower bar, and not being supported by any other means. Four screws on each gauge

were then adjusted so that they would touch four points, two on each bar near its extremities. By applying these gauges to the bars when in position, either in contact with each other or with a disc between, it is therefore easy to make the required adjustment of the cut surfaces.

The surfaces were now amalgamated, the amalgamated surfaces brought together, and experiments made on the distribution of temperature throughout the bar, to test the efficiency of the mercury contact. When the bar was uncut, the difference of temperature observed between the points in the middle, 1·05 cm. apart, was, as a mean of three experiments, ·76° C. With the cut bar and the mercury contact, the distribution of temperature in the other parts of the bars being the same, the difference of temperature observed was ·64° C. The cutting and grinding of the bar had reduced the distance between the points of observation to ·88 cm., hence if the mercury contact has no appreciable resistance the fall should be $\frac{\cdot 76 \times \cdot 88}{1 \cdot 05} = \cdot 65°$, which is, within the limits of error, what was observed. Hence, as far as the distribution of temperature along the bar is concerned, the mercury contact secures practical continuity. Occasional tests were made during the course of the work to see if this continued to hold. The resistance of the contact was found to increase slightly. Three tests made at the end of the work gave ·78° as the difference of temperature. This is equivalent to an increase of distance between the points of observation from ·88 cm. to 1·06 cm., and is probably caused by the gradual soaking of the mercury into the brass. Account is taken of this in the following calculations.

The conditions of the above experiments are not quite the same as in experiments with crystals, &c., for while in the above there is only one mercury film, in the crystal experiments there are two. To investigate the effect of this, a thin film of mica, about ·0003 cm. thick, was inserted. Although there are then two films of mercury and a film of mica between the bars, no change could be detected in the difference of temperature of the observing points. The same held on insertion of a piece of platinum foil ·0025 cm. thick. The corrections for the short length of bar and mercury contact between the points at which the temperatures are observed

and the surfaces of the discs, can, therefore, be determined from the observation with the amalgamated ends of the bars in contact.

In preparing the apparatus for an experiment, the bars and framework were placed so that the bars were vertical, with the cool bar at the top. The bars were taken out of the frame and the holes and contacts cleaned with dilute nitric acid, provided with mercury, washed, and then dried by filter paper. The hot bar was then inserted into lower part the frame, and if a disc was to be experimented on, it was placed on the mercury surface and the excess of mercury forced from under it. In the case of a transparent disc it was possible to see that the mercury formed a perfect mirror. The cool bar was then put into the upper part of the frame, and held up, in contact with the centre screw at the top of the frame, by means of a spring. The amalgamated end would be thus brought about ·5 cm. above the upper surface of the disc. It was then supplied with mercury, which hung down as a pendent drop. The upper screw was then turned till the end of the upper bar was about ·5 mm. from the upper surface of the disc. In this position the gauges were applied to the bars, and the loops so adjusted by means of the screws at their ends, that the four points of each gauge touched the bars. The upper screw was then rotated till the upper bar came into contact with the disc, and the excess of mercury was forced out. The frame was then placed over the water tank with the bars horizontal, and connections made to the steam and water supplies. The apparatus was allowed to stand about one and a half hours, in order that the distribution of temperature might become steady before observations were taken. Almost invariably on taking the bars apart at the conclusion of an experiment, the discs were found to adhere to the cool bar, and in the case of transparent discs this enabled it to be seen if the contact between the cool bar and the disc had been good. It was generally found as good a mirror as the contact between the hot bar and the disc. Some experiments were however made to try the effect of making contacts which were poor as far as could be judged by the appearance of the mirrors. No difference could be detected in the observations between an optically good and a bad mirror, so that a few experiments, in which the contacts were optically defective, have been included in the results given.

Reduction of Observations with Discs.

We have seen that the temperature throughout any short length of the bar may be represented by the empirical equation $v = \mathrm{A}\cosh \alpha x + \mathrm{B}\sinh \alpha x$. We assume that this equation holds for the first three observations on each side of the disc, and thus have, if x_1, x_2, x_3 are the co-ordinates of the points of observation, measured from the surface of the disc, and v_1, v_2, v_3 the observed temperatures,

$$\left.\begin{aligned} v_1 &= \mathrm{A}\cosh \alpha x_1 + \mathrm{B}\sinh \alpha x_1 \\ v_2 &= \mathrm{A}\cosh \alpha x_2 + \mathrm{B}\sinh \alpha x_2 \\ v_3 &= \mathrm{A}\cosh \alpha x_3 + \mathrm{B}\sinh \alpha x_3 \end{aligned}\right\}$$

These three equations are sufficient to fix the values of the constants A, B, α, but their solution is difficult unless $x_3 - x_2 = x_2 - x_1$. This relation is very nearly satisfied by the points of observation, in the hot bar, $x_2 - x_1 = 10{\cdot}56$ cms. $x_3 - x_2 = 10{\cdot}44$ cms.; in the cool bar, $x_2 - x_1 = 10{\cdot}51$ cms. $x_3 - x_2 = 10{\cdot}48$ cms.

The error introduced by assuming each of these intervals $= 10{\cdot}5$ cms. is small enough to be neglected in the cool bar, but a small correction is necessary in the case of the hot bar.

If dv_2/dx be the value of dv/dx at the point x_2 we have for the temperature v_2' at the point $x_1 + 10{\cdot}5$,

$$v_2' = v_2 - {\cdot}06\,\frac{dv_2}{dx}.$$

Now dv_2/dx is found to differ little from 1 for any of the experiments,* and we may, therefore, with sufficient accuracy, take $v_2' = v_2 - {\cdot}06$.

---

* The value of dv_2/dx may be determined as follows. By Taylor's Theorem we have—

$$f(x + l) - f(x) = lf'(x) + \frac{l^2}{2} f''(x) + \frac{l^3}{3} f'''(x) + \&c.$$

$$f(x) - f(x - l) = lf'(x) - \frac{l^2}{2} f''(x) + \frac{l^3}{3} f'''(x) + \&c.$$

Therefore $$\frac{f(x + l) - f(x - l)}{2l} = f'(x) + \frac{l^2}{3} f'''(x).$$

Putting $v = f(x)$ we have, since for any short length of the bar $\frac{d^2v}{dx^2} = a^2v$,

$$f'''(x) = \alpha^2 f'(x).$$

Therefore $$f'(x) = \frac{f(x + l) - f(x - l)}{2l\left(1 + \frac{l^2\alpha^2}{6}\right)}$$

The value $\frac{1}{6}(l^2\alpha^2)$ for this point of the bar is in all the experiments approximately ·04

Making use of v_2' we have from the three temperatures, v_1, v_2', v_3

$$\cosh \alpha l = \frac{v_1 + v_3}{2v_2'},$$

where $l = x_2 - x_1 = x_3 - x_2$, &c. This equation determines α from any three observations of temperature. The mean of the values thus determined for different points along the bars and for different experiments is used in the subsequent work.

We have then the equations

$$\left.\begin{aligned} v_1 &= \mathrm{A} \cosh \alpha x_1 + \mathrm{B} \sinh \alpha x_1 \\ v_2 &= \mathrm{A} \cosh \alpha x_2 + \mathrm{B} \sinh \alpha x_2 \end{aligned}\right\}$$

where $\cosh \alpha x_1$, $\sinh \alpha x_1$, $\cosh \alpha x_2$, $\sinh \alpha x_2$ are known quantities, to determine the values of A and B.

Differentiating the equation $v = \mathrm{A} \cosh \alpha x + \mathrm{B} \sinh \alpha x$ and putting $\alpha = 0$, we have at the surface in contact with the disc, $v = \mathrm{A}$, $dv/dx = \alpha \mathrm{B}$.

The isothermal surfaces in the discs themselves may be assumed to be planes, for a small calculation, like that made (p. 12) for the bar itself, shows that the radius of curvature of these surfaces is about 40 cms. Writing a_1, a_2 for the co-ordinates of the surfaces of the disc, A_1, A_2 the temperatures determined as above, Q_1, Q_2 the values of $k_1 \alpha \mathrm{B}$ in the bars at the surfaces in contact with the disc k_1 being the conductivity of bars, and k that of the disc, we have for the temperature in the disc itself:

$$v = \frac{\mathrm{A}_2 \sinh \sqrt{\frac{ph}{qk}} \cdot \sqrt{x - a_1} + \mathrm{A}_1 \sinh \sqrt{\frac{ph}{qk}} \cdot \sqrt{a_2 - x}}{\sinh \sqrt{\frac{ph}{qk}} \sqrt{a_2 - a_1}}.$$

Differentiating and writing down the expressions for the flow of heat into and out of the disc we have the equations:

$$\mathrm{Q}_1 q_1 = qk \sqrt{\frac{ph}{qk}} \cdot \frac{\mathrm{A}_2 - \mathrm{A}_1 \cosh \sqrt{\frac{ph}{qk}} \sqrt{a_2 - a_1}}{\sinh \sqrt{\frac{ph}{qk}} \sqrt{a_2 - a_1}},$$

and

$$\mathrm{Q}_2 q_1 = qk \sqrt{\frac{ph}{qk}} \frac{\mathrm{A}_2 \cosh \sqrt{\frac{ph}{qk}} \sqrt{a_2 - a_1} - \mathrm{A}_1}{\sinh \sqrt{\frac{ph}{qk}} \cdot \sqrt{a_2 - a_1}}$$

where p, h, q, k refer to the disc and have the usual meanings, q being $= q_1$ in most cases, differing only slightly in others.

Now $a_2 - a_1$, the thickness of the discs, is small enough to make $\sqrt{\frac{ph}{qk}}\overline{a_2 - a_1}$ small. Hence, writing $a_2 - a_1 = t$, and expanding the hyperbolic functions, we have, as a close approximation:

$$q_1 Q_1 = qk\sqrt{\frac{ph}{qk}}\,\frac{A_2 = A_1\left(1 + \frac{ph}{qk}\cdot\frac{t^2}{2}\right)}{\sqrt{\frac{ph}{qk}}\cdot t\left(1 + \frac{ph}{qk}\cdot\frac{t^2}{6}\right)}.$$

Therefore

$$k = \left(\frac{q_1}{q}\right)\cdot\frac{Q_1 t\left(1 + \frac{ph}{qk}\cdot\frac{t^2}{6}\right)}{A_2 - A_1\left(1 + \frac{ph}{qk}\cdot\frac{t^2}{2}\right)};$$

similarly

$$k = \left(\frac{q_1}{q}\right)\cdot\frac{Q_2 t\left(1 + \frac{ph}{qk}\cdot\frac{t^2}{6}\right)}{A_2\left(1 + \frac{ph}{qk}\cdot\frac{t^2}{2}\right) - A_1};$$

either of which equations determines k, the conductivity of the disc, if its approximate value is substituted in the terms involving t^2. The value of h used is that for a painted surface, at the mean temperature of the disc, and the value of $\frac{ph}{qk}t^2$ is given with sufficient accuracy for the above substitution by the equation

$$\frac{ph}{qk}t^2 = \cdot00056\frac{A_2 - A_1}{Q}t.$$

Observations.*

I. Transparent Isotropic Bodies.—The temperatures given are the means of three experiments.

Crown Glass Disc, 1·93 cm. diam., ·169 cm. thick. Air, 16 ·2 C.

Cool bar.	Hot bar.
v_1 8·58 A_1 8·83	v_1 18·44 A_2 18·25
v_2 4·20 Q_1 ·1365	v_2 26·54 Q_2 ·1336
$\therefore k_1 = \frac{\cdot1365\times\cdot169\times1\cdot001}{18\cdot25-8\cdot83\times1\cdot003} = \cdot00246$	$k_2 = \frac{\cdot1336\times\cdot169\times1\cdot001}{18\cdot25\times1\cdot0038-8\cdot83} = \cdot00241$

k mean = ·00244

* The results are collected in a table on page 30.

Flint Glass Disc, 1·93 cm. diam., ·177 cm. thick. Air, 16°·6 C.

Cool bar.	Hot bar.
v_1 7·60 A_1 7·83 v_2 3·54 Q_1 ·1254 $\therefore k = \frac{\cdot1254\times\cdot177\times1\cdot002}{18\cdot84-7\cdot83\times1\cdot006} = \cdot00203$	v_1 19·02 A_2 18·84 v_2 26·80 Q_2 ·1246 $k_2 = \frac{\cdot1246\times\cdot177\times1\cdot002}{18\cdot84\times1\cdot006-7\cdot83} = \cdot00199$

k mean = ·00201.

Rock Salt Disc, 1·95 cm. diam., ·83 cm. thick. Air, 15° C.

Cool bar.	Hot bar.
v_1 9·24 A_1 9·50 v_2 4·61 Q_1 ·1457 $k_1 = (\cdot98)\frac{\cdot1457\times83\times1\cdot005}{18\cdot22-9\cdot50\times1\cdot014} = \cdot0138$	v_1 18·47 A_2 18·22 v_2 27·31 Q_2 ·1515 $k_2 = (\cdot98)\frac{\cdot1515\times\cdot83\times1\cdot005}{18\cdot22\times1\cdot014-9\cdot50} = \cdot0138$

k mean = ·0138.

II. Crystals.—Temperatures, means of three experiments.

Quartz Disc, 1·91 cm. diam., 1·005 cm. thick. Thermal stream lines parallel to optical axis. Air, 15°·1 C.

Cool bar.	Hot bar.
v_1 10·09 A_1 10·50 v_2 4·64 Q_1 ·1680 $k_1 = (1\cdot02)\frac{\cdot168\times1\cdot005\times1\cdot003}{16\cdot40-\cdot105\times1\cdot010} = \cdot0298$	v_1 16·69 A_2 16·40 v_2 26·28 Q_2 ·1763 $k_2 = (1\cdot02)\frac{\cdot1763\times1\cdot005\times1\cdot003}{16\cdot40\times1\cdot010-10\cdot5} = \cdot0299$

k mean = ·0299.

Quartz Disc, 1·93 cm. diam., ·811 cm. thick. Thermal stream lines perpendicular to optical axis. Air, 16°·2 C.

Cool bar.	Hot bar.
v_1 9·09 A_1 9·39 v_2 4·07 Q_1 ·1545 $k_1 = \frac{\cdot1545\times\cdot811\times1\cdot004}{17\cdot45-9\cdot36\times1\cdot011} = \cdot01574$	v_1 17·71 A_2 17·45 v_2 26·86 Q_2 ·1616 $k_2 = \frac{\cdot1616\times\cdot811\times1\cdot004}{17\cdot45\times1\cdot011-9\cdot36} = \cdot01589$

k mean = ·0158.

ICELAND Spar Disc, 1·91 cm. diam., ·70 cm. thick. Thermal stream lines parallel to optical axis. Air, 16°·4 C.

Cool bar.	Hot bar.
v_1 7·82 A_1 8·10	v_1 18·73 A_2 18·49
v_2 3·36 Q_1 ·1436	v_2 27·41 Q_2 ·1478
$k_1=(1{\cdot}02)\frac{\cdot1436\times\cdot7\times1{\cdot}004}{18{\cdot}49-8{\cdot}10\times1{\cdot}013}=\cdot01001$	$k_2=(1{\cdot}02)\frac{\cdot1478\times\cdot7\times1{\cdot}004}{18{\cdot}49\times1{\cdot}013-8{\cdot}10}=\cdot00998$

k mean = ·0100.

ICELAND Spar Disc, 1·93 cm. diam., ·602 cm. thick. Thermal stream lines perpendicular to optical axis. Air, 16°·3 C.

Cool bar.	Hot bar.
v_1 7·95 A_1 8·12	v_1 18·61 A_2 18·37
v_2 3·33 Q_1 ·1405	v_2 27·31 Q_2 ·1475
$k_1=\frac{\cdot1405\times\cdot602\times1{\cdot}004}{18{\cdot}37-8{\cdot}12\times1{\cdot}012}=\cdot00837$	$k_2=\frac{\cdot1475\times\cdot602\times1{\cdot}004}{18{\cdot}37\times1{\cdot}012-8{\cdot}12}=\cdot00852$

k mean = ·00845.

MICA, large plate, ·18 cm. thick. Thermal stream lines perpendicular to cleavage planes. Air, 15°·6 C.

Cool bar	Hot bar
v_1 6·36 A_1 6·58	v_1 18·90 A_2 18·67
v_2 2·77 Q_1 ·1093	v_2 27·44 Q_2 ·1436
$k_1=\frac{\cdot1093\times\cdot18\times1{\cdot}002}{18{\cdot}67-6{\cdot}58\times1{\cdot}05}=\cdot00164$	$k_2=\frac{\cdot1436\times\cdot18\times1{\cdot}002}{18{\cdot}67\times1{\cdot}05-6{\cdot}58}=\cdot00199$

k mean = ·00181.

As the mica was in the form of a large plate, the above method of finding k is not strictly correct, and this accounts for the difference between the calculated values of k_1 and k_2. It was found impossible to use a disc, as in the other experiments, on account of the mica splitting. The value of k given must be taken as approximate only.

III. Rock Specimens.

Marble Disc, 1·93 cm. diam., ·26 cm. thick. The marble was the white variety used for statues. Air, 15°·5 C.

Cool bar.	Hot bar.
v_1 10·15 A_1 10·40	v_1 17·31 A_2 17·01
v_2 4·38 Q_1 ·1767	v_2 27·27 Q_2 ·1839
$k_1 = \frac{\cdot 1767 \times \cdot 26 \times 1 \cdot 001}{17 \cdot 01 - 10 \cdot 4 \times 1 \cdot 003} = \cdot 00699$	$k_2 = \frac{\cdot 1839 \times \cdot 26 \times 1 \cdot 001}{17 \cdot 01 \times 1 \cdot 003 - 10 \cdot 4} = \cdot 00718$

k mean = ·00709.

Slate Disc, 1·93 cm. diam., ·31 cm. thick, cut from an ordinary school slate. Air, 14°·9 C.

Cool bar.	Hot bar.
v_1 8·80 A_1 9·08	v 19·40 A_2 19·15
v 4·27 Q_1 ·1508	v_2 28·58 Q_2 ·1581
$k_1 = \frac{\cdot 1508 \times \cdot 31 \times 1 \cdot 002}{19 \cdot 15 - 9 \cdot 08 \times 1 \cdot 006} = \cdot 00468$	$k_2 = \frac{\cdot 1581 \times \cdot 31 \times 1 \cdot 002}{19 \cdot 15 \times 1 \cdot 006 - 9 \cdot 08} = \cdot 00482$

k mean = ·00475.

IV. Various Bodies Constantly Used in Physical Work.

Where no diameter is given the plate is of irregular shape, and rather larger than the section of the bars.

Shellac Plate, ·068 cm. thick. Air, 14°·2 C.

This plate was made between two microscope slides having plane surfaces. One slide was placed horizontal, and the upper surface covered with a smooth sheet of tinfoil. On the foil was laid a sufficient number of the thin films of shellac supplied by varnishmen to make a plate of the requisite size and thickness. The slide was then warmed gently from underneath till the shellac was soft, and the cold slide brought down on to the soft mass. In order to get the requisite thickness, and the surfaces of the plate parallel to each other, the two slides were kept apart by

two short lengths of wire ·068 cm. diameter laid across the lower slide near its ends, the upper slide being pressed against these. The tinfoil which attaches itself to the plate is readily dissolved off by mercury. This method is very convenient and gives excellent plates.

Cool bar.	Hot bar.
v_1 7·16 A_1 7·40 v_2 3·32 Q_1 ·1183 $k_1 = \frac{\cdot1183 \times \cdot068 \times 1\cdot001}{20\cdot76 - 7\cdot40 \times 1\cdot002} = \cdot000604$	v_1 20·95 A_2 20·76 v_2 28·74 Q_2 ·1159 $k_2 = \frac{\cdot1159 \times \cdot068 \times 1\cdot001}{20\cdot76 \times 1\cdot002 - 7\cdot40} = \cdot000589$

k mean = ·000596.

Paraffin Plate, ·038 cm. thick. Air, 13°·4 C.

This plate was made by dropping a little melted paraffin on to the cold upper surface of the lower slide, and placing the upper slide on it as described above. The cold surfaces are sufficient to ensure the paraffin being detachable from the glass.

Cool bar.	Hot bar.
v_1 8·90 A_1 9·19 v_2 4·49 Q_1 ·1378 $k_1 = \frac{\cdot1378 \times \cdot038 \times 1\cdot0002}{17\cdot87 - 9\cdot19 \times 1\cdot0006} = \cdot000604$	v_1 18·10 A_2 17·87 v_2 26·48 Q_2 ·1407 $k_2 = \frac{\cdot1407 \times \cdot038 \times 1\cdot0002}{17\cdot87 \times 1\cdot0006 - 9\cdot19} = \cdot000615$

k mean = ·000610.

Para Rubber, pure. Sheet ·0264 cm. thick. Air, 13°·8 C.

Cool bar.	Hot bar
v_1 9·00 A_1 9·26 v_2 5·01 Q_1 ·1401 $k_1 = \frac{\cdot1401 \times \cdot0264 \times 1\cdot0002}{19\cdot00 - 9\cdot26 \times 1\cdot0005} = \cdot000380$	v_1 19·23 A_1 19·00 v_2 27·87 Q_2 ·1433 $k_2 = \frac{\cdot1433 \times \cdot0264 \times 1\cdot0002}{19\cdot00 \times 1\cdot0005 - 9\cdot26} = \cdot000388$

k mean = ·000384

Sulphur Plate, ·0584 cm. thick. Air, 14°·2 C.

This plate was made in the same way as the plate of shellac, except that it was found better to use a sheet of tinfoil on the surface of each slide.

Cool bar.	Hot bar.
v_1 6·60 A_1 6·83 v_2 3·08 Q_1 ·1082 $k_1 = \frac{·1082 \times ·0584 \times 1·0007}{20·74 - 6·83 \times 1·002} = ·000455$	v_1 20·92 A_2 20·74 v_2 28·42 Q_2 ·1085 $k_2 = \frac{·1085 \times ·0584 \times 1·0007}{20·74 \times 1·002 - 6·83} = ·000455$

k mean = ·000455.

Ebonite Disc,* 1·93 cm. diam., ·0414 cm. thick. Air, 14°·9 C.

Cool bar.	Hot bar
v_1 7·35 A_1 7·61 v_2 3·36 Q_1 ·1227 $k_1 = \frac{·1227 \times ·0414 \times 1·0004}{20·10 - 7·61 \times 1·0013} = ·000407$	v_1 20·30 A_2 20·10 v_2 28·16 Q_2 ·1202 $k_2 = \frac{·1202 \times ·0414 \times 1·0004}{20·10 \times 1·0013 - ·701} = ·000398$

k mean = ·000403.

Gutta-Percha Sheet, ·0617 cm. thick. Air, 14°·4 C.

This sheet was made of the material used for insulating wire. A small quantity was cut from a wire, melted, and pressed into a sheet between the two cold microscopic slides.

Cool bar.	Hot bar.
v_1 5·97 A_1 6·19 v_2 2·35 Q_1 ·1087 $k_1 = \frac{·1087 \times ·0617 \times 1·0006}{20·76 - 6·19 \times 1·002} = ·000461$	v_1 20·94 A_2 20·76 v_2 28·40 Q_2 ·1076 $k_2 = \frac{·1076 \times ·0617 \times 1·0006}{20·76 \times 1·002 - 6·19} = ·000456$

k mean = ·000458.

* Kindly supplied to me by Mr C H. Gray, of the Silvertown Company.

PAPER Disc, 1·93 cm. diam., ·019 cm. thick. Air, 15 ·4 C.

This was cut from an ordinary visiting card.

Cool bar.	Hot bar.
v_1 9·42 A_1 9·73 v_2 4·56 Q_1 ·1515 $k_1 = \frac{\cdot1515\times\cdot019\times1\cdot0001}{18\cdot81-9\cdot73\times1\cdot0003} = \cdot000317$	v_1 19·05 A_2 18·81 v_2 27·91 Q_2 ·1496 $k_2 = \frac{\cdot1496\times\cdot019\times1\cdot0001}{18\cdot81\times1\cdot0003-9\cdot73} = \cdot000313$

k mean = ·000315.

"ASBESTOS Paper" Disc, 1·93 cm. diam., ·047 cm. thick.

Air, 14°·9 C.

This was the ordinary asbestos millboard of commerce. It consists of paper to the pulp of which sufficient asbestos has been added to render it incombustible.

Cool bar.	Hot bar.
v_1 8·40 A_1 8·68 v_2 4·02 Q_1 ·1358 $k_1 = \frac{\cdot1358\times\cdot047\times1\cdot0004}{19\cdot93-8\cdot68\times1\cdot001} = \cdot000568$	v_1 20·16 A_2 19·93 v_2 28·67 Q_2 ·1368 $k_2 = \frac{\cdot1368\times\cdot047\times1\cdot0004}{19\cdot93\times1\cdot001-8\cdot68} = \cdot000571$

k mean = ·000570.

MAHOGANY Disc, 1·93 cm. diam., ·056 cm. thick, cut from a sheet of "veneer" used by cabinet makers. Air, 15 ·9 C.

Cool bar	Hot bar
v_1 6·67 A_1 6·89 v_2 3·06 Q_1 ·1107 $k_1 = \frac{\cdot1107\times\cdot056\times1\cdot0006}{20\cdot57-6\cdot89\times1\cdot002} = \cdot000454$	v_1 20·75 A_2 20·07 v_2 28·51 Q_2 ·1167 $k_2 = \frac{\cdot1167\times\cdot056\times1\cdot0006}{20\cdot57\times1\cdot002-6\cdot89} = \cdot000477$

k mean = ·000465

Walnut Disc, 1·93 cm. diam., ·069 cm. thick, cut from a sheet of "veneer." Air, 16° C.

Cool bar.	Hot bar.
v_1 5·11 A_1 5·29 v_2 2·14 Q_1 ·0917 $k_1 = \frac{·0917 \times ·069 \times 1·001}{22·46 - 5·29 \times 1·004} = ·000363$	v_1 22·60 A_2 22·46 v_2 29·52 Q_2 ·0888 $k_2 = \frac{·0888 \times ·069 \times 1·001}{22·46 \times 1·004 - 5·29} = ·000358$

k mean = ·000360.

Cork Disc, 1·93 cm. diam., ·05 cm. thick, cut by a section-cutting machine from a sound cork. Air, 15°·1 C.

Cool bar.	Hot bar.
v_1 2·22 A_1 2·33 v_2 ·34 Q_1 ·0530 $k_1 = \frac{·0530 \times ·05 \times 1·002}{23·30 - 2·33 \times 1·005} = ·000127$	v_1 23·39 A_2 23·30 v_2 29·10 Q_2 ·0547 $k_2 = \frac{·0547 \times ·05 \times 1·002}{23·30 \times 1·005 - 2·33} = ·000130$

k mean = ·000129.

Silk Sheet, ·0084 cm. thick. This was cut from a dress-piece of plain brown silk. Air, 16°·4 C.

Cool bar.	Hot bar.
v_1 10·06 A_1 10·39 v_2 4·95 Q_1 ·1600 $k_1 = \frac{·16 \times ·0084}{16·76 - 10·39} = ·000210$	v_1 17·03 A_2 16·76 v_2 26·35 Q_2 ·1690 $k_2 = \frac{·169 \times ·0084}{16·76 - 10·39} = ·000223$

k mean = ·000216.

Silk Sheet, ·017 cm. thick, cut from a piece of ribbed silk ribbon. The thickness given is the mean of that across ribs and across grooves. Air, 16°·6 C.

Cool bar.	Hot bar.
v_1 8·03 $\quad$ A_1 8·30 v_2 3·72 $\quad$ Q_1 ·1333 $k_1 = \frac{\cdot1333 \times \cdot017}{18\cdot65 - 8\cdot30} = \cdot00022$	v_1 18·88 $\quad$ A_2 18·65 v_2 27·37 $\quad$ Q_2 ·1415 $k_2 = \frac{\cdot1415 \times \cdot017}{18\cdot65 - 8\cdot30} = \cdot00023$

k mean = ·00023.

Cotton Sheet, ·085 cm. thick. A piece of thick tape. Air, 16°·4 C.

Cool bar.	Hot bar.
v_1 5·23 $\quad$ A_1 5·43 v_2 1·95 $\quad$ Q_1 ·100 $k_1 = \frac{\cdot100 \times \cdot085 \times 1\cdot001}{21\cdot24 - 5\cdot43 \times 1\cdot004} = \cdot000539$	v_1 21·41 $\quad$ A_2 21·24 v_2 28·79 $\quad$ Q_2 ·1044 $k_2 = \frac{\cdot1044 \times \cdot085 \times 1\cdot001}{21\cdot24 \times 1\cdot004 - 5\cdot43} = \cdot000557$

k mean = ·00548.

Flannel Sheet, ·1 cm. thick. Air, 15°·1 C.

Cool bar.	Hot bar.
v_1 2·34 $\quad$ A_1 2·44 v_2 ·59 $\quad$ Q_1 ·0504 $k_1 = \frac{\cdot0504 \times \cdot1 \times 1\cdot006}{24\cdot58 - 2\cdot44 \times 1\cdot018} = \cdot000229$	v_1 24·67 $\quad$ A_2 24·58 v_2 30·39 $\quad$ Q_2 ·0505 $k_2 = \frac{\cdot0505 \times \cdot1 \times 1\cdot006}{24\cdot58 \times 1\cdot018 - 2\cdot44} = \cdot000225$

k mean = ·000227.

As the silk, cotton, and flannel yield somewhat, the measurements of thickness are not very accurate in these three cases. The error will be greatest in the cases of flannel and cotton, and probably small in the case of silk.

Table of Results.

Material and direction of stream lines.	Thermal conductivity between 25° and 35° C. C.G.S. units.		Refractive Index.
Copper	..	·7 to ·8 Lorenz, F. Weber, &c.	
Brass	..	·25 to ·3 Lorenz, Neumann, &c.	
Brass bar used	·27		
Bismuth	..	·017 Lorenz	
Mercury	..	·018 Angström	
Crown glass	·00243	·0016 H. Meyer	1·53
Flint glass	·00201	·0014 ,,	1·64
Glass	..	·0021 Peclet ·0005 G. Forbes	
Rock salt	·0138	·016 Tuschmidt	1·55
Quartz along axis	·0299	·026 Tuschmidt ·001 G. Forbes	1·55
,, perpendicular to axis	·0158	·016 Tuschmidt ·004 G. Forbes	1·56
Iceland spar along axis	·0100	·016 Tuschmidt	1·66
,, perpendicular to axis	·0084	·0086 ,,	1·49
Mica perpendicular to cleavage	·0018	.. ..	1·57
White marble	·0071	·0075 Peclet ·0073 Yamagawa ·0011 G. Forbes	
Slate	·0047	·0008 ,,	
Water	..	·0015 Winkelmann	
Glycerine	..	·0007 ,,	
Olive oil	..	·0004 F. Weber	
Shellac	·00060		
Paraffin	·00061	·00014 G. Forbes	
Pure Para rubber	·00038		
Rubber	..	·00046 Peclet	
Vulcanised rubber	..	·00009 G. Forbes	
Sulphur	·00045		
Ebonite	·00040	·00008 ,,	
Gutta-percha	·00046		
Paper	·00031	·00045 G. Forbes	
Asbestos paper	·00057		
Mahogany across fibre	·00047		
Walnut across fibre	·00036		
Cork	·00013		
Silk	·00022		
Cotton	·00055		
Flannel	·00023		

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In the foregoing table the conductivities of a few metals and liquids are given in order to show the position of the bodies experimented on amongst other conductors.

Where experiments have been previously made by other experimenters their results are given for comparison.

Such comparison shows a fair degree of concordance between the present results and those obtained by totally different methods, with the exception of the results of G. Forbes, which were obtained by the following method. A can about 9 cms. diameter was filled with a freezing mixture, placed on a sheet of the material the conductivity of which was to be determined, and the lower surface of the sheet brought down on to a surface of water at 0° C. Ice is formed on the surface of the sheet, and Forbes works out an expression for the thickness of this ice in terms of the temperature of the freezing mixture (which was observed by a thermometer placed in it), the thickness of the material, the time, and the conductivities of ice and the material. In working out this expression, however, he assumes the conductivity of the materials between the thermometer in the freezing mixture and the upper surface of the sheet to be infinitely great, which, when one considers the layers of liquid, metal, and air present, is scarcely justifiable. On this account almost all Forbes's results are low.

Peclet's results for metals were all found to be low, and this led to the assumption that all his results were the same. It is, however, evident from the present experiments that his results for bad conductors are correct. This is probably owing to the fact that the layers of still water which, in his experiments, adhered to the surfaces of the sheet experimented on, are of much less importance when the sheet is a bad conductor.

Tuschmidt's results are obtained by a method which Weber used for liquids. The sheet of liquid is simply replaced by one of the crystal, the contacts being made by means of glycerine. As glycerine has a conductivity which is only about $\frac{1}{20}$th of those of the crystal plates, the glycerine layers have a great effect on the flow of heat through the plates. This is a defect of the method, and, in addition, the plates themselves must be large, and are therefore expensive. Tuschmidt's results and those of the present paper agree fairly, the only great difference being in the case of Iceland spar along the axis.

Meyer's determinations depend on the rate of rise of the temperature of a calorimeter, into which a heated cube of the material is plunged. It is questionable whether the assumption which he makes, that the temperature of the surface of the cube at any instant is that given by the thermometer in the calorimeter, is justifiable on account of the difficulty of preventing a layer of water adhering to the surface. The same objection applies to the method which he used to confirm the results obtained by his first method.

Remarks.

From the Table of Results it is at once evident that, for transparent bodies, no such comparison between thermal conductivity and velocity of propagation of light can be made, as has been made by Kundt for the metals. The thermal conductivities vary enormously for very small change of refractive index, and the variations are sometimes in the same direction as the variation of the index of refraction, sometimes in opposite. It is remarkable that the bodies quartz and rock salt, which are diathermanous bodies, should also be good thermal conductors, quartz being a better conductor than bismuth. To prove that the high value of the conductivity is not due to heat passing through these bodies by radiation from the hot bar to the cold, several experiments were made with the apparatus arranged as it was during the experiment in quartz, but the quartz disc was removed, thus allowing the hot bar to radiate heat through the intervening air space to the cool bar. Under these conditions no change of temperature at the point of observation near the end of the cool bar could be detected when the hot bar was suddenly

cooled. As air is a more diathermanous body than quartz, it is thus evident that the amount of heat radiated through the quartz from one bar to the other is too small to affect the above results.

The high conductivity of quartz would render the use of fused quartz (the conductivity of which does not probably differ much from that of quartz crystal) advantageous for vessels subject to sudden change of temperature, and for delicate thermometers.

The results for Iceland spar and marble seem to indicate that the irregular arrangement of the crystals in marble interferes with the passage of heat.

Water and salt solutions have conductivities about equal to that of glass.

The solid insulations used in electrical work rank with glycerine and the oils, so far as thermal conductivity is concerned.

Silk has about one-third the conductivity of shellac. Hence, if a silk-covered wire has the covering saturated with shellac, it will have its heat conducted away to surrounding bodies much faster than previously. The practice of soaking galvanometer coils in shellac is, therefore, good from a thermal point of view, as it enables the heat generated in the wire to pass more rapidly to the exterior of the coils, and be radiated away.

On account of the low conductivity of paraffin, standard resistance coils with temperature co-efficients ought not to be embedded in paraffin, as the B.A. standard is.

Cork is the worst conductor experimented on.

Almost all the substances experimented on are insulators electrically. Although tables of their electrical conductivities are available, the values given seem to depend more on the condition of the surface of the body experimented on than on its material, and, on this account, it is of little use to make any comparisons between the electrical and the thermal conductivities of these substances.

The above experiments were carried on in the Physical Laboratory of the Owens College.

ON THE LAW OF COOLING, AND ITS BEARING ON CERTAIN EQUATIONS IN THE ANALYTICAL THEORY OF HEAT.

By Charles H. Lees, M.Sc. *(Bishop Berkeley Fellow at the Owens College).*

(From the Philosophical Magazine.)

ALTHOUGH it is a well-known fact that the temperature of a heated body allowed to cool in air does not follow "Newton's law," it has been usual to assume that law to hold in cases in which the loss of heat of a body through contact of its surface with air had to be taken into account. In calorimetry the error thus introduced is probably small; but it becomes of much greater importance in those methods of determining thermal conductivity in which the ratio of the outer to the inner conductivity of the body is a quantity determined experimentally, and this ratio used in conjunction with a value of the outer conductivity* (supposed to follow Newton's law) to determine the inner conductivity.

The method to which I specially refer is that of Briot, Despretz, &c., in which a bar of the substance whose conductivity is required is placed in a horizontal position in air, and heated at one end. The equation of motion of heat in the bar is then, assuming the isothermal surfaces to be planes,

$$c\rho\frac{\delta v}{\delta t}=\frac{\delta}{\delta x}\left(k\frac{\delta v}{\delta x}\right)-\frac{p}{q}.hv\,; \quad . \quad . \quad . \quad . \quad . \quad (1)\dagger$$

* The "*Conductibilité extérieure*" of Fourier, or the surface emissivity of Thomson, art. "Heat," *Encyc. Brit.*, p. 577.

† Fourier, *Théorie Analytique de la Chaleur*. Thomson, "Collected Papers," vol. ii, p. 42, or *Encyc. Brit.*, art. "Heat," p. 579.

where v = excess of temperature at a point x of bar above temperature of air, which is supposed constant; c = specific heat, ρ = density, k = inner conductivity, h = outer conductivity, at temperature excess v; p = perimeter of section of bar; q = area of section of bar.

Assuming, with Fourier, that c, ρ, k, h are constant, we have for the "steady state" the equation

$$\frac{\delta^2 v}{\delta x^2} = \frac{ph}{qk} \cdot v;$$

the solution of which is

$$v = Ae^{\sqrt{\frac{ph}{qk}} \cdot x} + Be^{-\sqrt{\frac{ph}{qk}} \cdot x},$$

where A and B are constants of integration. By determining the temperature at different points of a bar thus heated, the value of $\sqrt{\frac{ph}{qk}}$ can be found. Briot and Despretz determined the temperature by means of thermometers placed in holes in the bars. This would, on account of the different conductivities of the bars and the glass and mercury of the thermometers, make the isothermal surfaces deviate considerably from planes. The results, however, of both experimenters show evidence of an increase of $\sqrt{\frac{ph}{qk}}$ with temperature, especially where the bars are of the poorer conducting metals, and the effects of the holes therefore less. This is also the case with the results of Wiedemann and Franz, who determined the temperature by means of a thermo-junction brought into contact with the surface of the bar at different points.

From the experiments which follow it will be seen that h increases about 50 per cent. as the temperature varies from 30° C. to 80° C., while k and c for a metal are not found to vary more than about 5 per cent. in the same interval. The most important source of error in the assumptions of Fourier is, then, that introduced by the variation of h, and it is towards a more accurate determination of this variation that the following experiments have been conducted *.

* The experiments were carried out in the Owens College Physical Laboratory

A bar of infinite length originally heated to a uniform temperature would, if allowed to cool in air, continue to satisfy the condition $\frac{\delta v}{\delta x}=0$, and it will be assumed that for the bars used in these experiments this is still the case. Since the temperature has previously been assumed constant throughout any section perpendicular to the axis, this amounts to assuming the temperature uniform throughout the whole bar. The equation (1) then takes the form

$$c\rho\frac{\delta v}{\delta t}=-\frac{p}{q}.h.v.$$

Or, multiplying both sides of equation by l, the length of the bar, and writing more generally for v on right side $f(v)$,

$$c\rho\, lq\frac{\delta v}{\delta t}=-plh.f(v).$$

Or, writing m for ρlq, and s for the whole surface of the bar, including the two ends,

$$cm\frac{\delta v}{\delta t}=-s.h.f(v) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The bars used in these experiments to determine the form of $f(v)$ were about 26 or 27 cms. long and 1·9 cm. diameter. They were nickel-plated, so as to give them the same smooth even surface. At the extremities of a diameter in the middle of the length of the bars, two small holes, about ·7 mm. diameter and 2·5 mms. deep, were bored, and into them an iron and a German-silver wire respectively were soldered. The other ends of these wires dipped into mercury cups, in the circuit of an aperiodic Wiedemann's galvanometer. The mercury cups being provided with thermometers, the arrangement formed a thermo-circuit, and from the deflexion of the galvanometer and the temperature of the mercury cups the temperature of the bar at any time could be found. The deflexion was read off by means of a telescope and scale situated 2·5 metres from the galvanometer. The correction of the extreme deflexion for the assumption $\tan 2\theta=2\tan\theta$ is less than ·3 per cent. and is neglected. The bars were at first suspended horizontally in the room by means of two threads, and the temperature of the air observed by means of a thermometer situated vertically under the bar and protected from radiation by a small paper screen. On account of the air currents

in the room, and the "lag" of the thermometer indications behind the actual temperatures of the air, the cooling was ultimately carried out in a water jacket 55 cms. diameter and 75 cms. long. The change of temperature of the jacket was then slow and regular, and the correction for this change could easily be applied. The bars were heated in an air bath surrounded by water at 100° C. for three or four hours, and at the end of that time the temperatures of bath and mercury cups, the deflexion, and the resistance of the circuit were determined. The resistance was ascertained by shunting into circuit a known resistance, and observing the diminution of deflexion. These observations give data for reducing the observations of deflexion and resistance during cooling to degrees Centigrade. During cooling observations of deflexion were taken every two minutes; of resistance, and of temperatures of water jacket and mercury cups, every four minutes.

Writing e for the product of the deflexion and resistance, v temperature of junction in bar, v_1 temperature of mercury cups, $\bar{e}$, $\bar{v}$ values of e, v when bar is in hot bath, C some constant, we have, according to Avenarius*, for an iron-German-silver circuit,

$$e = \mathrm{C}(v - v_1)\left(1 - \cdot00034(v + v_1)\right),$$

$$\bar{e} = \mathrm{C}(\bar{v} - v_1)\left(1 - \cdot00034(\bar{v} + v_1)\right);$$

$$\therefore\ v - v_1 = (\bar{v} - v_1)\,\frac{e}{\bar{e}}\cdot\frac{1 - \cdot00034(v + v_1)}{1 - \cdot00034(\bar{v} + v_1)}$$

$$= \frac{\bar{v} - v_1}{\bar{e}}\cdot e\left(1 - \cdot00034(\bar{v} - v)\right) \text{ approx.}$$

Writing for v, in correcting factor, its approximate value $\frac{e}{\bar{e}}\bar{v}$, we have

$$v - v_1 = \frac{\bar{v} - v_1}{\bar{e}}\cdot e\left(1 - \cdot00034\,\bar{v}\,\frac{\bar{e} - e}{\bar{e}}\right),$$

which determines $(v - v_1)$, in Centigrade degrees, from observation of deflexions and resistance.

By applying this equation to the observations made, we get a series of temperatures of the bar at two-minute intervals; and from this series the form which $f(v)$ must have to best represent the variation of the outer conductivity is to be found. We consider only simple forms of $f(v)$, so as to complicate equation (1) as little as possible, and commence with the simplest.

* *Pogg. Ann.* cxxii, p. 199.

The simplest form is $f(v) \equiv v$, the usual assumption. Substituting in (2), we deduce

$$\int \frac{dv}{v} + at = \text{C}, \text{ where } a = \frac{sh}{cm} \text{ (C is an arbitrary constant),}$$

or

$$v = v_0 e^{-at}, \qquad \text{where } v_0 \text{ is value of } v \text{ at time } t = 0.$$

If a in this equation be determined from the first eight minutes of the curve of cooling, when the mean temperature excess of the bar was about 64° C., it is always 30 or 40 per cent. greater than a determined from the last eight minutes when the temperature excess was 11° C. Hence a increases with the temperature, and we are led to the assumption :—$f(v) \equiv v(1+bv)$*, which gives

$$\int \frac{dv}{v(1+bv)} + at = \text{constant},$$

or

$$\frac{1}{v} + b = \text{A}e^{at}, \quad \text{where A is an arbitrary constant.}$$

The constants of this equation, determined from observations at times 0, 10, 20 minutes, are in one experiment

$$a = \cdot 0277, \quad b = \cdot 0047, \quad \text{A} = \cdot 0187 ;$$

and at 40, 50, 60 minutes, in the same experiment,

$$a = \cdot 0221, \quad b = \cdot 0165, \quad \text{A} = \cdot 0284.$$

A similar variation was found in other cases, so that the cooling is not well represented by making $f(v)$ a quadratic function of v.

Ceasing to consider integral powers of v, we write

$$f(v) \equiv v(a + bv^m),$$

where m is some ± quantity. This gives as integral,

$$v^{-m} + \frac{b}{a} = \text{C}e^{amt}.$$

Solving this by trial we find $m = \cdot 2$ approx. and $a = 0$; and we deduce as probable form $f(v) \equiv v^n$, where $n > 1$.

The equation (2) therefore takes the form :—

$$cm\frac{\delta v}{\delta t} = -sh \, . \, v^n ; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2')$$

or the rate of loss of heat from the bar varies as the nth power of the excess of temperature of bar above temperature of air, supposed to remain constant, where $n = 1 \cdot 2$ approximately.

* Kundt and Warburg (*Pogg. Ann.* clvi) make use of this to express the cooling of a thermometer in a sphere concentric with its bulb. H. F. Weber (*Mon. Ber. d. Berlin Akad.* 1880) considers some correction of this form to be necessary in dealing with conductivities of bars.

So far the specific heat c has been considered constant; but the form of (2′) allows its variation to be taken into account without materially affecting the integration. Writing

$$c = c_0(1 + c'v),$$

where c_0 is the value of c at the temperature of the air in the experiments (about 17° or 18° C.), and c' is some constant, generally less than ·001, (2′) becomes

$$mc_0(1 + c'v)\frac{\delta v}{\delta t} = -sh.v^n.$$

Another small correction has to be applied for the change of temperature of the water jacket, which up to the present has been assumed constant. Writing it now $= V$, where V is a function of t such that its value at the end of the experiment $= 0$, we have

$$mc_0(1 + c'v)\frac{\delta v}{\delta t} = -sh(v - V)^n.$$

From the tables which follow, it will be seen that V/v is generally less than $\frac{1}{100}$; so that if, in the left-hand side of the above equation, $1 + c'(v - V)$ be substituted for $1 + c'v$, the error introduced is generally less than $\frac{1}{10000}$. Also from these tables it is seen that, for an interval of twenty minutes, $\frac{\delta V}{\delta t}$ is with close approximation $= -q\frac{\delta v}{\delta t}$, where q is generally less than $\frac{1}{100}$. Hence, for an interval of twenty minutes, we have as a very close approximation,

$$\frac{\delta v}{\delta t} - \frac{\delta V}{\delta t} = \frac{\delta v}{1 + q\delta t},$$

or

$$\frac{\delta v}{\delta t} = \frac{1}{1 + q} \cdot \frac{\delta v - V}{\delta t};$$

and the equation of cooling corrected for all known variations becomes

$$\frac{mc_0(1 + c'v - V)}{1 + q} \cdot \frac{\delta v - V}{\delta t} = -sh(v - V)^n;$$

or

$$\int \left\{(v - V)^{-n} + c'(v - V)^{1-n}\right\} dv + \frac{sh(1 + q)}{mc_0} t = \text{constant};$$

or

$$(v - V)^{1-n}\left(1 - \frac{n - 1}{2 - n}c'(v - V)\right) = \frac{sh(1 + q)(n - 1)}{mc_0} t + C. \quad . \quad (3)$$

Tables follow from which it can be seen how this equation agrees with experiment.

Nickel-plated Copper Bar Cooled in Water Jacket.

t, minutes.	V°C.	$(v-V)$ C.	$(v-V) = \cdot 21\left(1 - \frac{n-1}{2-n}\frac{c'v-V}{s}\right)$.	$20\frac{sh\,1+q\,n-1}{mc_0}$.	$20\frac{sh\,n-1}{mc_0}$.	$\frac{sh\,n-1}{mc_0}$.	
0	16·97	73·4	·4040				
2	17·05	68·1	102			Means	
4		63·3	168			of 5.	
6	·15	58·8	236				
8		54·62	299				
10	·21	50·83	366				
12		47·35	434				
14	·27	44·19	499				Another exp. gave
16		41·28	567				
18	·31	38·54	633				
20		36·06	700	·0660	·0653		
22	·35	33·67	770	68	61		
24		31·60	835	67	60		
26	·36	29·71	896	60	54		
28		28·00	958	59	53	·003281	·003264
30	·38	26·26	·5028	62	57		
32		24·61	096	62	57		
34	·39	23·06	167	68	63		
36		21·82	227	60	56		
38	·39	20·60	292	59	55	3288	3232
40		19·39	358	58	54		
42		18·40	425	55	52		
44		17·34	489	54	52		
46	·39	16·39	550	54	52		
48		15·50	621	53	52	3262	3209
50		14·65	685	57	56		
52		13·90	751	55	54		
54	·39	13·15	815	48	48		
56		12·47	883	56	56		
58		11·88	943	51	51	3265	3247
60		11·26	·6008	50	49		
62	·40	10·69	079	54	53		
64		10·16	141	52	51		
66		9·67	206	56	55		
68		9·19	273	52	51	3259	3272
70	·40	8·76	337	52	51		
72		8·36	399	48	47		
74		7·95	467	52	50		
76		7·58	531	48	46		
78	·42	7·26	592	49	47	3241	3220
80		6·93	654	46	44		
					Mean...	·003266	·003240

$n = 1{\cdot}21.$ $c_0 = {\cdot}092.$

$m = 676$ grams. $c' = {\cdot}000231.$

$s = 163{\cdot}4$ sq. cms.

$$\therefore \frac{h}{c_0} = {\cdot}00325 \times \frac{1}{{\cdot}21} \times \frac{676}{163{\cdot}4} = \mathbf{{\cdot}0640.}$$

Nickel-plated Iron Bar Cooled in Water Jacket.

t, minutes.	V° C.	$(v-V)$° C.	$(v-V)-\cdot21\left(1-\frac{n-1}{2-n}\frac{c'v-V}{\ }\right)$.	$20\frac{sh}{mc_0}\frac{1+q}{n-1}$.	$20^{n}\frac{sh}{mc_0}\frac{n-1}{\ }$.	$\frac{sh}{mc_0}\frac{n-1}{\ }$.	
0	18·36	74·77	·3965			Means	
2	·44	69·78	·4031			of 5.	
4		65·10	094				
6	·57	60·72	159				
8		56·74	223				
10	·67	53·04	291				
12		49·73	348				
14	·72	46·92	404				
16		43·70	474				
18	·78	40·92	540				Another exp. gave
20		38·42	603	·0638	·0631		
22	·81	36·02	669	38	31		
24		33·91	731	37	30		
26	·85	31·88	795	36	29		
28		30·00	858	35	28	·003149	·003198
30	·87	28·28	920	29	23		
32		26·67	983	35	30		
34	·89	25·09	·5049	45	40		
36		23·78	108	34	29		
38	·93	22·55	169	29	24	3136	3187
40		21·25	236	33	28		
42	·96	20·00	305	36	31		
44		19·02	363	32	27		
46	·98	17·91	431	36	30		
48		16·96	495	37	30	3146	3161
50	·99	16·16	552	32	25		
52		15·27	621	38	31		
54	19·01	14·51	682	33	26		
56		13·79	745	37	30		
58	·03	13·06	815	36	29	3141	3147
60		12·41	875	39	32		
62	·03	11·84	934	29	22		
64		11·25	·6000	37	31		
66	·03	10·71	062	31	26		
68		10·20	127	32	28	3139	3180
70	·03	9·79	179	27	23		
					Mean..	·003139	·003179

n 1·21 c_0 ·112 $\therefore h$ ·00316 573·4
m 573·4 grams. c' ·00101. c_0 ·21 162·2
s 162·2 sq. cms. **·0520.**

NICKEL-PLATED ZINC BAR * COOLED IN WATER JACKET.

t, minutes.	V° C.	$(x-V)$° C.	$(x-V)-21\left(1-\frac{n-1}{2}c'\overline{x-V}\right)$.	$20\frac{sh\,1+q\,n-1}{mc_0}$.	$20\frac{sh\,n-1}{mc_0}$.	$\frac{sh\,n-1}{mc_0}$.	
0	17·00	70·93	·4050			Means of 5.	
2	·10	64·92	122				
4		59·02	215				
6	·20	54·01	297				
8		49·33	381				
10	·24	45·10	466				
12		41·29	553				
14	·27	37·98	637				
16		35·00	717				
18	·29	32·33	798				Another exp. gave
20		29·95	877	·0827	·0820		
22	·29	27·70	964	42	37		
24		25·59	·5045	30	25		
26	·29	23·69	126	29	24		
28		21·99	211	30	26	·004132	·004100
30		20·30	301	35	33		
32		18·98	374	21	19		
34	·29	17·77	447	10	08		
36		16·60	531	14	12		
38		15·42	614	16	15	4087	4087
40		14·43	693	16	16		
42	·29	13·50	777	13	13		
44		12·62	862	17	17		
46		11·83	946	20	20		
48		11·05	·6031	20	20	4086	4109
50	·29	10·41	108	07	07		
52		9·79	185	11	11		
54		9·22	268	21	21		
56		8·62	353	22	22		
58		8·08	440	26	26		
60	·29	7·64	517	24	24	4093	4112
					Mean..	·004100	·004102

$n = 1{\cdot}21.$ $c_0 = {\cdot}0915.$
$m = 573{\cdot}4$ grams. $c' = {\cdot}000485.$
$s = 165{\cdot}5$ sq. cms.

$$\therefore \frac{h}{c_0} = \frac{{\cdot}00410}{{\cdot}21} \times \frac{573{\cdot}4}{165{\cdot}5} = \mathbf{{\cdot}0676.}$$

* Nickel surface not good, peeled in places.

The constancy of the numbers in the columns of first differences (the columns headed $20\,\frac{sh\overline{n-1}}{mc_0}$) shows how well the assumption that the rate of loss of heat varies as the nth power of the temperature excess can be made to represent the actual fact by a proper choice of n. Within the limits of the experiments, *i.e.*, 80° to 10° C. temperature excess, there is no definite secular change of the mean values of $\frac{sh\overline{n-1}}{mc_0}$, and we thence conclude that the above law is a close approximation to the actual fact.

The values of h/c_0 deduced from the experiments are, for copper, iron, and zinc, respectively ·0640, ·0520, ·0676, where h is the amount of heat lost from 1 sq. cm. of the surface in 1 minute, when the temperature excess is 1° C.* and temperature of air is about 18° C., and c_0 is the specific heat of the material of the bar at 18° C.

Taking the specific heats at 18° C. as ·092, ·112, ·0915 respectively,† and dividing by 60, we have for the amount of heat lost in 1 second under the above conditions :—

·0000981, ·0000971, ·000103.

On account of the uncertainty of the specific heat values, and the fact that the zinc bar had not so good a surface as the others, not much weight is to be attached to the differences between these three results. The value deduced from the copper bar is probably nearest the truth ; and we have then the loss of heat in 1 second from 1 sq. cm. of surface of the bars used equal to ·000098 $(v-\mathrm{V})^{1\cdot21}$ heat units.

The particular value 1·21 of the index n refers only to the cooling in the water jacket, but it seems not to depend to any great extent on the presence or not of the jacket, for when the cooling was performed in the middle of the room at a considerable

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* That is, if the loss of heat varies for temperatures below 10° C. excess, as it is found to do from 80° to 10° C. excess

† Naccari gives :— Cu ·092, Fe ·106, Zn ·0915 } *Beibl.* xii, p. 326.

The values for Cu and Zn agree with the results of other experimenters, but that for Fe is too low. Brystrom's value = 112 is taken. Naccari's values for c' have been used in each case

distance from any object the value of n which best represented the cooling was less than 1·21 but greater than 1·2.

The value of n is, however, dependent on the nature of the surface, and also on the cross section of the bar; for by covering the iron bar with a shining black varnish n was reduced to about 1·16. The varnish was, however, slightly softened at the highest temperature, so that the character of the surface would change somewhat during the cooling.

The much larger square nickel-plated bars used by Mitchell in his repetition of Forbes's experiments on conductivity give for the cooling experiment $n = 1{\cdot}26$ (*see* p. 47). This increase of n may be due to change of form of section, or to change in dimensions, as both these circumstances affect the stream lines* produced in the air by the presence of the heated bars. It seems probable, however, that the only part of the loss of heat which is altered by alteration of the nature of the surface, is that part due to radiation.

From these facts we conclude that the loss of heat from an element of surface of heated bar, due to the effects of radiation, conduction, and convection into the surrounding air, is proportional to the nth power of the excess of temperature of that element above that of the surrounding air.

The fundamental equation for the state of heat along such a bar becomes then:—

$$c\rho\frac{\delta v}{\delta t} = \frac{\delta}{\delta x}\left(k\,\frac{\delta v}{\delta x}\right) - \frac{p}{q}.hv^n. \quad . \quad . \quad . \quad . \quad (1')$$

It is evident from this equation what a great effect the outer conductivity has on the nature of the solution of the problem of motion of heat in a bar. The solution in terms of exponentials for the steady state used by Despretz,† Wiedemann and Franz,‡ and others is replaced by a power of the temperature, and the solution for the "steady periodic" state first given by Angström§ no longer holds. The above solutions neglect also variations of k, and we proceed to consider the effect of this.

* See for stream lines, Lodge, *Phil. Mag.* xvii, p. 214 (1884); Rayleigh, *Proc. R. S.*, Dec., 1882.

† *Ann. de Chim. et de Phys.* xix et xxxvi.

‡ *Pogg. Ann.* lxxxix.

§ *Ibid.* cxiv, cxviii, cxxiii.

Taking the case in which the temperature state is steady, we have the equation

$$\frac{\delta}{\delta x}\left(k_r \frac{\delta v}{\delta x}\right) - \frac{p}{q} h v^n = 0 ; \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or taking k_r as a linear function of the temperature, thus,

$$k_r = k_0 + k' v,$$

we have, on expanding the equation (4),

$$(k_0 + k' v) \frac{\delta^2 v}{\delta x^2} + k' \left(\frac{\delta v}{\delta x}\right)^2 - \frac{p}{q} h v^n = 0. \quad . \quad . \quad . \quad (5)$$

As the term in $\left(\frac{\delta v}{\delta x}\right)^2$ is often neglected in the mathematical treatment of conductivity*, it is interesting to compare its value, as deduced from experiment, with the first term of the above equation.

Taking Mitchell's figures for his iron bar,† we deduce

	Value of 1st term.	Value of 2nd term.
At 50° C. excess .	·011 (5·5) = ·06	·00001 (2500) = ·025
,, 100° ,, .	·011 (13) = ·14	·00001 (12,000) = ·12

From which it is evident that the neglect of the second term will seriously affect the results, unless k' is very small, *i.e.*, the conductivity nearly independent of the temperature. In the above case the conductivity has been taken as changing 10 per cent. in 100° C., which, according to the experiments of Forbes,‡ Kirchhoff and Hausemann,§ Lorenz,‖ and others, is by no means an extreme case.

Those determinations of conductivity which involve the assumptions $k' = 0$, $n = 1$, need not be considered, as the results derived from them can only be rough approximations. Integrating (4) with respect to x, between the limits x_1 and x_2, we have

$$q \Big/ k_r \frac{\delta v}{\delta x} \Big/_{x_2}^{x_1} = \int_{x_2}^{x_1} p\, h v^n . dx ; \quad . \quad . \quad . \quad . \quad . \quad (6)$$

or the difference between the amount of heat flowing along the bar at points x_1, x_2 is the amount of heat lost from the sides between the two points.

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* The effect of this will be to raise the value of the conductivity as deduced from experiment.

† *Trans. R. S. E.*, 4 July, 1887.

‡ *Trans. R. S. E.* xxiii, xxiv.

§ *Wied. Ann.* ix, xiii. Kirchhoff and Hausemann neglect, however, the second term in equation (5).

‖ *Ibid.* xiii.

If there be no "source or sink" along the bar except at the origin, and the bar be long enough to make $\frac{\delta v}{\delta x}=0$ at its end, we have

$$qk_v\frac{\delta v}{\delta x}=\int_{\infty}^{x} phv^n dx, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which determines k_v from observations of v along the bar.

We have then in (7) the solution of the problem of determination of conductivity by the bar method, free from the most serious of the errors involved in the usual assumptions. The outstanding assumption is that of plane isothermal surfaces.

To confirm the deductions made in this paper, from the fact that the loss of heat from a heated bar is proportional to a power of the temperature excess, I proceed to apply them to the observations of Mitchell,* who has repeated Forbes's experiments on conductivity, after having the bars used by Forbes nickel-plated. He gives the values of $-\frac{\delta v}{\delta t}$ for different temperature excesses for an iron bar; and from this the following table is calculated :—

Temp. excess in degrees Cent.	$-\frac{\delta v}{\delta t}$.	c_v specific heat. $c_0=1$.	$-c_v\frac{\delta v}{\delta t}$.	$v^{1\cdot26}$.	$c_v\frac{\delta v}{\delta t}\Big/v^{1\cdot26}$
10	·11	1·01	·1111	18·19	·0611
20	·26	1·021	·2655	43·56	10
30	·43	1·031	·4433	72·61	10
40	·61	1·041	·635	104·5	10
50	·807	1·052	·849	138·4	14
60	1·00	1·062	1·062	173·9	07
70	1·19	1·072	1·276	211·2	05
80	1·405	1·082	1·521	248·9	11
90	1·605	1·092	1·755	289·8	06
100	1·83	1·103	2·018	331	10
110	2·04	1·113	2·270	373·4	08
120	2·28	1·124	2·563	417·6	14
200	4·4	1·206	5·307	792·5	·0670
250	6·12	1·258	7·699	1051	·0733

The constancy of the quotient $c_v\frac{\delta v}{\delta t}\Big/v^{1\cdot26}$ up to a temperature excess of over 100° C. shows how well the index 1·26 represents the cooling in this case. Above 100° C. n appears to increase.

* *Trans. R. S. E.*, 4 July, 1887.

Putting $n = 1{\cdot}26$ in (7), the equation determining k from the observation of temperatures along such a bar heated at one end is

$$qk_v \frac{\delta v}{\delta x} = \int_x^\infty phv^{1{\cdot}26}\,dx.$$

Mitchell gives v and $-\frac{\delta v}{\delta x}$ at different points along the bar, and from these we have the following table :—

x in feet	v.	$-\frac{\delta v}{\delta x}$	$v^{1{\cdot}26}$	$\int_x^\infty v^{1{\cdot}26}\,dx$.	$\frac{\int_x^\infty v^{1{\cdot}26}\,dx}{\frac{\delta v}{\delta x} x k_v}$.
·25	172·1	195·4	656·3	446	2·28
·5	125·25	132·2	439·7	311	2·35
·75	92·3	92	299·4	220	2·39
1·25	52·0	47·9	145·3	113	2·36
1·75	30·35	29·2	73·7	60·8	2·09
2·25	18·2	15·2	38·7	33	2·18
2·75	11·15	10	20·9	19·2*	1·92
3·75	4·3		6·16		
4·75	1·85		2·27		
5·75	·7		·96		

The numbers given in the last column indicate a rise of conductivity with temperature, which agrees with the result given by Mitchell as his most reliable. As the integration

$$\int_x^\infty v^{1{\cdot}26}\,dx$$

is performed graphically, no great importance is to be attached to small variations of results. The number 2·28 ought to be increased about 5 per cent., as the index 1·26 in the cooling experiment only holds up to about 100° C. temp. excess. A close agreement of the values of k with one another is probably not to be expected, on account of the deviation of the isothermal surfaces from planes caused by the insertion of the thermometers into the bar. The method of Forbes would be much improved in this respect if the temperatures were determined by thermo-junctions either set in the bar at different points, or movable, such as Wiedemann and Franz used.

* Liable to an error of about 5 per cent. on account of uncertainty of cooling, &c., below 10° C. excess.

Finally, then, in the general theory we have the equation of continuity in the form

$$c_v\rho\frac{\delta v}{\delta t}=\frac{\delta}{\delta x}\left(k_v\frac{\delta v}{\delta x}\right)+\frac{\delta}{\delta y}\left(k_v\frac{\delta v}{\delta y}\right)+\frac{\delta}{\delta z}\left(k_v\frac{\delta v}{\delta z}\right)$$

with the condition at surfaces in contact with gas

$$k_v\frac{\delta v}{\delta n_1}+hv''=0,$$

where n can only be taken $=1$ when temperature changes of only a few degrees occur, but where c_v and probably k_v may be taken as constant when changes of temperature of not more than 50° C. occur.

ON THE DETERMINATION OF THE THERMAL CONDUCTIVITIES OF BAD CONDUCTORS.

By CHARLES H. LEES, M.Sc. (*Bishop Berkeley Fellow at the Owens College*).

(From the Memoirs of the Manch. Lit. and Phil. Society.)

THE experiments of Senarmont and others* have shown that anisotropic bodies possess different thermal conductivities in different directions, and that in the majority of transparent bodies the conductivity in any direction increases as the index of refraction of light in that direction decreases. The methods by which these results have been obtained, differ little from that of Senarmont, which depended on the melting round a central heated point of a thin layer of wax, previously spread over the surface of a crystal. In general, the area melted is an ellipse, the ratio of the axes of which is equal to the square root of the ratio of the conductivities along them. Such methods, therefore, give no information with respect to the absolute values of the conductivities, and a glance at the different results obtained in successive experiments on the same crystal shows that even the comparative values cannot be trusted, except as rough approximations.

The recent determination by Prof. Kundt of the indices of refraction† of a number of metals, and the fact that he finds they

* References may be found in any text book, *e.g.*, Wüllner, *Lehrbuch der Experimentalphysik* iii, p. 310.

† Strictly we can only speak of an index of refraction of a substance when Snell's law $\sin i/\sin r = \text{constant}$, is obeyed. Kundt therefore defines the index for a metal as the limit when $i=0$ of $\sin i/\sin r$. The recent experiments of du Bois and Rubens (*Phil. Mag.* [5] xxx, 365) have shown that for iron, cobalt, and nickel, Snell's law is approximately true, but that there is considerable deviation from it in silver and gold.

stand in the same order with respect to velocity of transmission of light and thermal conductivity, make it important to determine the conductivities of crystals in different directions with greater accuracy and in absolute measure, in order to compare different crystals with each other. At the suggestion of Prof. Kundt, I commenced some time ago at Strasburg a series of experiments with this end in view. Although these experiments are not yet completed, I propose in this paper to give a short account of the methods tried and the approximate results obtained.

The desirableness of dealing with small pieces of crystals, and the impossibility of making temperature observations in the crystals themselves, point at once to placing a thin plate of a crystal between the ends of two bars of metal, one heated and the other cooled at the ends away from the plate, and observing the temperature along each bar. These observations, if the conductivity of the bars were known, would furnish data for a determination of the conductivity of the crystal.

Difficulties arise, however, from the imperfect nature of the contacts between metal and crystal. Lodge* proposed to improve them by inserting pads of tinfoil, but this I found not to answer. Eventually a metal which would amalgamate was used for the bars, and the amalgamated ends made contact extremely well.

As the bars and crystal lose heat by convection, conduction, and radiation to the surrounding air, a method (that of Angström) was first tried which gives by one experiment both the internal and external conductivities. One end of the arrangement of bars and crystal was alternately heated for six minutes by steam and cooled for six minutes by water till the temperature throughout was a periodic function of the time.

If

v = excess of temp. at point x over that of air
q = area of section of bar
p = perimeter of section of bar
ϱ = density
c = specific heat, k = internal conductivity } supposed constant
h = external conductivity supposed to follow Newton's law

* Prof. O. Lodge proposed in 1878 (*Phil. Mag.* [5] v, p. 110) to determine the conductivities of crystals by the above method, but I am not aware that he has published any results.

the equation to the motion of heat in the bar, the isothermal surfaces being supposed plane, is

$$c\varrho\frac{\partial v}{\partial t}=k\frac{\partial^2 v}{\partial x^2}-\frac{p}{q}h.v. \quad \ldots \quad (1)$$

the steady periodic solution of which is:

$$v=\mathcal{F}(x)+\sum_{n=1}^{\infty}A_n c^{-\mu_n x}\cos 2n\pi\left(\frac{t}{\mathrm{T}}-\frac{x}{\lambda_n}+a_n\right) \quad \ldots \quad (2)$$

where T = period, A, μ, λ are constants and

$$\left.\begin{aligned} k&=\frac{c\varrho\lambda_n}{2\mathrm{T}\mu_n}\cdot \\ h&=\frac{c\varrho}{2\mathrm{T}}\left(\lambda_n\mu_n-\frac{4n^2\pi^2}{\lambda_n\mu_n}\right) \end{aligned}\right\} \quad \ldots \quad (3)$$

From these equations it is evident that observations of temperatures at two points of one bar give λ_n and μ_n and thence the internal and external conductivities of the bar, and observations at two points on opposite sides of the crystal plate and as close as possible to it, give similarly the conductivities of the crystal.

Temperatures were determined by three thermo-electric couples of iron and German silver wire soldered into the bars near the crystal, and in circuit with a galvanometer. By taking two additional thermo-junctions in the metal bar, the solution (2) was tested, and found not to represent the variation of temperature throughout the bar. I have since shown that this is to a great extent due to the great increase of h with the temperature,* and that Angström's solution (2) can only be taken as a rough approximation to the actual variation of temperature throughout the bar.

To get rid of this difficulty of the variation of h with the temperature, and at the same time to do away with the necessity for a knowledge of the values of c and ϱ for the crystal, I began experiments with the bars and crystal packed in a cylinder of sawdust, and used only the "steady state." The bars were of brass, 2 cms. diam. and 26 cms. long. The ends of each bar were amalgamated, and along the curved surface four thermo-junctions

* It is evident, moreover, that the solution (2) can only apply to a bar of infinite length heated and cooled at one end. For a finite bar, and especially for the case of a bad conductor interposed between two lengths of bar, it is necessary to add to the expression (2) a corresponding expression in which the sign of x is altered. This makes the calculation of k and h much more complicated.

of iron and brass wire were soldered, two being as near the ends as possible. The two bars were held in position within a vertical paper cylinder 8 cms. diam. by means of six set screws, which enabled the two amalgamated surfaces, between which the crystal disc was to come, to be set parallel. After putting in the crystal, the space between the bars and paper cylinder was packed with sawdust, the screws withdrawn, and contacts made at top and bottom with a water and a steam can respectively. The ends of the wires from the thermo-junctions came outside the paper cylinder, and could be put in succession in circuit with a galvanometer. Observations of deflections of the galvanometer and a previous determination of the constants of the junctions, give the temperatures at eight points of the bars, and from these the values of dv/dx below and above the crystal respectively can be calculated. These, combined with a knowledge of the conductivity k of the brass bar, give the flow of heat into and out of the crystal disc respectively through its plane surfaces. From the eight observations of temperature, the temperatures of the two surfaces of the crystal can also be found.* We thus have a determination of the conductivity of the crystal in a direction parallel to the axis of the disc by a method which follows very closely the definition of conductivity. If the sawdust were an absolute non-conductor, the method would agree exactly with the definition.

In the above the isothermal surfaces have been assumed plane and perpendicular to the axis of the bar, but in the experiments the temperature at five points of the outer cylinder were also determined, so that each experiment gives sufficient data for determining the distribution of heat throughout the whole space within the outer cylinder. I did not consider, however, that the accuracy obtained in the observations would warrant the carrying out of the calculations on these rigid lines, especially as no tables exist of one of the functions which enter into the calculation.†

* The main features only of the calculations are entered into here. In the actual calculation corrections are applied for the thin layer of mercury between the crystal and the bar, for the variation of dv/dx within the crystal, &c., the amount of these corrections being determined by special experiments.

† I refer to the Bessel's function of the second kind and zero order for unreal values of the argument.

The conductivity of the brass bar was determined by Forbes's method, with the modifications suggested by me in a previous paper.* Two experiments are necessary, one determining the outer and the other the relation between the outer and inner conductivity.

Cooling Experiments to determine the Outer Conductivity.

In these experiments one of the bars used in the crystal apparatus is heated to 100° in an air bath and then allowed to cool in air, the temperature being observed by thermo-junctions soldered to the middle of the bar.

Writing m for the mass of the bar cooled, s its surface, and assuming the temperature of the bar to be constant throughout, we can put (1) in the form

$$cm\frac{\partial v}{\partial t} = -sf(v)$$

where $f(v)$ is a function of v determined by experiment to be of the form hv^n where h and n are constants. If the temperature of the surrounding air is not constant the equation takes the form

$$cm\frac{\partial v}{\partial t} = -sh(v - \mathrm{V})^n$$

where V is the temperature of the air.

Multiplying both sides of this equation by dt and integrating we have

$$v - v_o = -\frac{sh}{cm}\int_{t_o}^{t}(v - \mathrm{V})^n dt$$

where v_o is the temperature at time t_o.

The following table gives the mean result of three experiments:—

* *Phil. Mag.* (5) xxviii, p. 442.

TABLE I.

Minutes t.	v	V	$(v-\mathrm{V})^{1\cdot17}$	$\int_{t=79}^{t}(v-\mathrm{V})^{1\cdot17}dt$	$\int_{t=79}^{t}(v-\mathrm{V})^{1\cdot17}dt/(v-v_{79})$
0	88·55° C	15.62° C	151·2	3281	MEANS.
2	82·50	15·51	136·9	2993	
4	77·08	15·48	124·1	2732	48·24
6	72·24	15·49	112·7	2495	
8	67·78	15·49	102·5	2280	
10	63·81	15·54	93·3	2084	
12	60·00	15·58	84·7	1906	
14	56·77	15·58	77·5	1744	48·08
16	53·78	15·56	71·0	1595	
18	50·93	15·58	64·8	1460	
20	48·29	15·59	59·1	1336	
22	45·92	15·59	54·2	1223	
24	43·84	15·61	49·8	1119	48·05
26	41·79	15·63	45·6	1023	
28	39·95	15·64	41·8	936	
30	38·25	15·64	38·4	855·5	
32	36·79	15·62	35·6	781·5	
34	35·29	15·59	32·7	713·2	48·22
36	34·00	15·59	30·2	650·3	
38	32·68	15·55	27·8	592·3	
40	31·65	15·52	25·9	538·7	
42	30·59	15·50	23·9	488·9	
44	29·64	15·44	22·3	442·7	48·63
46	28·72	15·40	20·7	399·7	
48	27·76	15·44	18·9	360·2	
50	27·05	15·40	17·7	323·6	
53	26·17	15·42	15·9	273·3	48·38
56	25·14	15·41	14·3	228·0	
59	24·31	15·47	12·8	187·3	
64	23·20	15·52	10·9	128·1	
69	22·13	15·53	9·1	78·2	47·79
74	21·24	15·47	7·8	36·0	
79	20·50	15·46	6·6		

MEAN 48·18

From this it is seen that the cooling is represented with great accuracy by the above equation if $n = 1{\cdot}17$, the specific heat of the bar being supposed constant.

We have $\frac{mc}{sh} = 48{\cdot}18$ (time in minutes).

Now $m = 644$ grams.

$c = {\cdot}092$

$s = 160$ sq. cms.

Hence $h = 000{,}128$ calories per sq. cm. per second for 1° C. excess.

Statical Experiments to determine k.

In these experiments the uncut bar of about one metre length is heated at one end, and the temperature along it in the "steady state" determined by means of thermo-junctions.

The equation (1) reduces for this experiment to the form

$$kq\frac{d}{dx}\left(k_v\frac{dv}{dx}\right)=\frac{p}{m}.\,h(v-\mathrm{V})^n$$

where k represents the conductivity at a temperature v; and V is the temperature of the air under any section.

Multiplying through by dx and integrating we have

$$q.\left/k_v\frac{dv}{dx}\right/_{x_2}^{x_1}=\int_{x_2}^{x_1}ph.\,(v-\mathrm{V})^n dx,$$

where x_1 x_2 are the co-ordinates of any two points on the bar.

The following table gives the mean of three experiments, the integration being performed by mechanical quadrature :—

Table II.

x	v	V	$(v-\mathrm{V})^{1\cdot47}$	$\int_0^x(v-\mathrm{V})^{1\cdot47}dx$	$\frac{dv}{dx}$	$\int_0^x(v-\mathrm{V})^{1\cdot47}dx+41$	$\left(\int_0^x(v-\mathrm{V})^{1\cdot47}dx+41\right)/\frac{dv}{dx}$	k_v
0	17·44 C.	16·05 C.	1·47		(·040)	41·0	985	(·26)
23·90	18·61	16·17	2·84	46·6	·0887	87·6	987	·262
45·73	21·34	16·20	6·79	145·5	·1888	186·5	988	·262
64·50	25·91	16·37	14·00	328·7	·3749	369·7	986	·261
79·98	33·39	16·50	26·69	628·5	·7084	669·5	945	·251
92·36	44·40	16·61	48·90	1080·2	1·228	1121·2	913	·242
107·15	57·32	16·67	76·31	1621·5	1·784	1662·5	932	·247
108·42	72·21	16·71	109·85	2243·1	(2·308)	2284·1	990	(·265)

The first and last numbers in the sixth and ninth columns are uncertain, as dv dx at the ends of the curve x, v can only be determined approximately.

From the approximate value of k, which can be obtained from the fifth and sixth columns of this table, the approximate value of $qk_r\frac{dv}{dx}$ when $x=0$ is determined to be 41. Hence column 7 is calculated; and the numbers in it are

$$=\left(qk.\frac{dv}{dx}\right)_{x=0}+\int_0^x ph(v-\mathrm{V})^n dx.$$

The numbers in the column headed k_r are calculated from the equation

$$k_r=\frac{ph\left\{\int_0^x(v-\mathrm{V})^{1\cdot17}dx+41\right\}}{q\frac{dv}{dx}}=\cdot000{,}265\,\frac{\int_0^x(v-\mathrm{V})^{1\cdot17}dx+41}{\frac{dv}{dx}}$$

Conductivities of Crown and Flint Glass.

Taking ·250 as the conductivity of the brass bars, the following results are deduced from several experiments on crown and flint glass discs, the temperatures in each disc being supposed represented by the equation $v=ax+bx^2$, the origin of x being taken at the cooler surface of the disc, and the temperature of that surface being taken as zero.

Crown Glass ·16 cm. thick.

x	v	$k_b\frac{dv}{dx}$
0	0	·222
·16	16·02	·250

$k_b\frac{dv}{dx}$ being the amount of heat which crosses a surface of contact of disc and bars, as calculated from the observations of temperatures in the bars.

From this I find k for crown glass = ·00235.

Flint Glass ·177 cm. thick.

x	v	$k_b\frac{dv}{dx}$
0	0	·211
·177	18·98	·234

From this I find k for flint glass = ·00208.

Taking the index of refraction of crown glass as about 1·5, and of flint glass as about 1·6, it is seen that the thermal conductivity of glass increases as its index of refraction diminishes, as Kundt found to be the case in metals.

The numbers ·00235 and ·00208 may be relied on to a greater degree relatively to each other than absolutely, owing to change of electromotive force of the thermo-junctions, produced by an unavoidable straining of the wires in packing the sawdust between the bars and the outer cylinder. On this account the apparatus has been modified, and I am at present engaged in re-determining the conductivities of the glass discs used in the above experiments, and in determining the conductivities of quartz and Iceland spar in different directions. The results of these experiments I hope shortly to communicate to the Society.

ON THE SPECIFIC HEAT OF NON-CONDUCTORS.

By W. W. Haldane Gee, B.Sc., *and*
Hubert L. Terry.

(From the Memoirs of the Manch. Lit. and Phil. Society.)

Part I.—Caoutchouc.

COMPARATIVELY few determinations have been made of the specific heat of non-conductors, and since a knowledge of this constant has become of some technical importance, we have made a number of experiments with different substances. The present paper will be devoted to Caoutchouc.

Fine Para rubber $\frac{1}{114}$ of an inch thick was generally used, and the following figures represent fairly its composition :—

Caoutchouc	96·83
Resin	1·25
Water	1·77
Soap, &c.	0·15
	100·00

Since the water is driven off when the rubber is heated to 100° C., the substance actually used contained about 98·5 % of caoutchouc and about 1·3 % of a material whose specific heat would be little different from that of caoutchouc. It may be considered, then, that we have been dealing with pure caoutchouc of the formula $(C_{10}H_{16})x$. For the supply of material and for assistance generally we are much indebted to Messrs. Chas. Macintosh & Co., Limited, of Manchester.

As Regnault's method of mixtures was employed, not much description of the process is necessary. At first sight the determination presents the difficulty that the rubber being an exceedingly

bad conductor of heat, the time of the mixture attaining its maximum temperature will be prolonged, and the correction for cooling large and its calculation uncertain. We find, however, by applying the correction formulæ, that the error from this source becomes unimportant, and certainly less than the errors incident to the variation in the composition of the substance, or to the difficulty of ascertaining its exact temperature when heated.

Description of Apparatus.

Calorimeter.

This was made of thin hard-rolled brass 62 mms. diam. and 152 mms. long. It was enclosed within an outer zinc can 120 mms. diam. and 188 mms. in depth, separated by corks. This zinc can was soldered to an outer can 200 mms. diam. and 255 mms. deep, which was filled with water. Finally, the whole was enclosed within a box packed with wool.

The outer can was provided with an annular stirrer, while the calorimeter had a smaller stirrer with a glass handle. A baize curtain divided the calorimeter from the heating apparatus.

Three different kinds of stirrers were used:—

(1) Perforated bucket of very thin sheet-brass with a wooden handle. The roll of rubber was dropped into this.

(2) A glass handle was fixed to a zig-zag piece of brass wire which was fixed in the rubber.

(3) A thermometer was fixed in the centre of the roll of rubber.

In the latter two cases the stirrer was also in the heating vessel.

Heating Apparatus.

In the earlier experiments a steam oven, having a constant temperature of 98° C., was employed. The rubber was enclosed in a wide test tube plugged with cotton wool, and surrounded with a cloth. Later we used a steam-jacketed copper vessel, into which the test tube fitted. The loss of material during the two hours' heating, starting with rubber exposed to a saturated atmosphere as tested by means of a hygrometer, amounted to 0·64 per cent.

Thermometers.

For the estimation of the temperature of the calorimeter two thermometers by Hicks were used:—

(1) No. 430296 had a range from 13° to 23° C., and was divided into tenths, each degree being about 25 mms.

Hence:—

$$1° = 25 \text{ mms.}$$
$$\cdot 1° = 2 \cdot 5 \text{ mms.}$$
$$\cdot 01° = \cdot 25 \text{ mm.}$$

a quantity which was readily estimated with the naked eye.

(2) No. 430298.

$$1° = 35 \text{ mms.}$$
$$\cdot 1° = 3 \cdot 5 \text{ mms.}$$
$$\cdot 01° = \cdot 35 \text{ mm.}$$

For ascertaining the temperature of the hot rubber, a thermometer divided into degrees whose boiling point had been determined, was used.

The temperature of the enclosure was ascertained by means of a thermometer by Heintz, estimating to ·01°.

Method of Experiment.

It was thought desirable to inter-roll the sheet of rubber with metallic foil, so as to hasten the time of cooling. This was accordingly done in most of the experiments, though we found afterwards that it lessened the time of mixture by no large amount. The foil employed throughout the experiments, though sold as "tin" foil, was found to contain 80 % of lead, and the determination of its specific heat gave as a mean of several estimations ·035, which value has been used in the calculations. In all cases the roll of rubber was completely encased in the foil, to prevent it sticking to the test tube in the heating chamber.

About 20 grams of rubber, as a rule, was employed. This was inter-rolled with the foil and heated for about two hours in the chamber described, and then quickly transferred to the calorimeter, the rubber being easily slipped out of the glass tube.

The readings of the temperature of the calorimeter were noted at half-minute intervals, the calorimeter being continuously stirred by hand.

Method of Calculation.

The following formula was used:—

$$s = \frac{W+K}{M} \cdot \frac{(\theta+C)-t}{T-(\theta+C)} - \frac{M'\sigma}{M}$$

where

M = mass of rubber.

M′ = ,, tinfoil.

W = ,, water in calorimeter.

K = water equivalent of calorimeter, stirrer, and thermometer.

T = temperature of the rubber.

t = initial temperature of the water.

θ = final temperature of the water.

σ = specific heat of the foil.

s = ,, ,, rubber.

The value of C, which represents the loss due to cooling, may be obtained from one of the three following formulæ:—

Correction Formulæ.

No. I.

Regnault-Pfaundler (*Ann. de Chim. et de Physique*, 4ᵉ Serie xi, p. 248, 1867).

In this formula a graphic method of correction is employed, or the formula

$$C = nv + \frac{r^1 - r}{t^1 - t}\left(\Sigma_{n-1}^{1}\,\theta + \frac{\theta_n + \theta_n}{2} - nt\right);$$

may be used instead.

where C is the quantity to be added to the observed maximum θ_n which is taken as that temperature after which the difference of the successive readings remains constant;

r = rate of loss of temperature before the introduction of the hot body into the calorimeter, the mean temperature being t.

r^1 = the corresponding quantity after the introduction of the hot body, and when the rate of cooling becomes constant, the mean temperature being t^1;

$\theta_0\ \theta_1\ \theta_2\ \ldots\ \theta_n$ are the observed temperatures at the successive time intervals from the time of introducing the hot body to that of obtaining the maximum.

No. II.

Pape (*Pogg. Ann.* cxx, p. 579, 1863) gives finally

$$C = \frac{V_m - V_1 + V_m \lambda_1 T}{V - V_m - V_m \lambda_1 T} S_1 ;$$

in which $$\lambda_1 = \frac{\log v_n - \log v_{n+1}}{\log e}$$

and

V_m = max. temperature of calorimeter.
V_1 = initial ,, ,,
V = temp. in heater.
T = time reaching maximum temperature.
S_1 = sp. ht. of fluid in calorimeter.
v_n and v_{n+1} being successive temperatures during the period of regular cooling.

Or, in its most approximate form, using the notation of the preceding formula,

$$C = n\theta \frac{\log \theta_m - \log \theta_{(m+1)}}{\log e}$$

where C is the quantity to be added to the actually observed maximum θ attained in n time intervals; whilst θ_m and $\theta_{(m+1)}$ are successively observed temperatures in the period during which the cooling is regular.

No. III.

Founded on the same differential equations used by Pape, Dr. Schuster has independently arrived at the following formula :—

$$C = \frac{\Delta\theta}{\Delta T} \cdot \frac{t_m - t_o}{t'' - t_o} \left[\frac{\sigma_1}{\sigma_2} \cdot \frac{t_m - t_0}{t' - t_0} T' + \theta_n \right];$$

where $\Delta\theta$ is the fall of temp. in time ΔT during the period of steady cooling at the temperature t''.

t_m = maximum temperature reached in n time intervals.

t_o = temperature of enclosure.

t' = observed temperature after a lapse of time T′ after the introduction of the hot body.

σ_1 and σ_2 = water values of the hot body and of the calorimeter and contents respectively.

θ_n = time of reaching maximum.

We now give an example where the value of C is calculated by these three different formulæ :—

Mass of rubber ... = 38·70
,, foil ... = 1·13
,, water ... = 299·2
K = 4·3.

Mass of perforated brass holder used as stirrer 12·30.

$t = 16°·97$
Room temp. 17°·5
$T = 99°$ after two hours' heating
Rise = 5°·03.

Thermometer in water to length of 3 inches.
The value of v was negligible.

Readings at half-minute intervals.

0	reading	...	...	$16·97 = \theta_0$
1	,,	...	...	$19·50 = \theta_1$
2	,,	...	...	$20·80 = \theta_2$
3	,,	...	...	$21·30 = \theta_3$
4	,,	...	...	$21·58 = \theta_4$
5	,,	...	...	$21·72 = \theta_5$
6	,,	...	...	$21·78 = \theta_6$
7	,,	...	...	$21·79 = \theta_7$
8	,,	...	...	$21·80 = \theta_8$
9	,,	...	...	$21·80 = \theta_n = \theta_9$
10	,,	...	..	21·79
14	,,	...	...	21·71
18	,,	...	...	21·62
20	,,	...	...	21·58
23	,,	...	...	$21·50 = \theta_m$
24	,,	...	...	$21·48 = \theta_{m+1}$
26	,,	...	...	21·44

Hence $v^1 = ·021$

Substituting these values in Pfaundler's formula we get, after simplifying,

$$C = \frac{·021}{4·65}\left(170·2 + 19·4 - 152·7\right),$$

whence $C = ·17,$

and substituting the above figures for the corresponding letters in Pape's formula we get

$$C = 9 \times 21·8 \frac{\log 21·5 - \log 21·48}{\log e},$$

whence $C = ·19$

and by Schuster's formula we get

$$C = \cdot 19.$$

We may here remark that this formula may be much simplified for our purpose by using the form

$$C = \frac{\Delta\theta}{\Delta T}\theta_n,$$

as the rest of the formula generally only affects the third place of decimals.

If now we take ·2° as the value of C, putting this value into Regnault's equation, we get in the above example

$$x = \frac{299\cdot2 + 4\cdot3}{38\cdot7} \cdot \frac{(21\cdot8 + \cdot2) - 16\cdot97}{99 - (21\cdot8 + \cdot2)} - \frac{\cdot75}{38\cdot7}$$

$$x = \cdot5123 - \cdot0194$$

$$= \cdot493$$

That the correction is a very necessary one is seen if we calculate the above, ignoring C, when we obtain for x the value 0·471. About the same value for C, viz., ·2°, was obtained by Pape and Pfaundler, in a large series of experiments made on various earths and salts.

The results agree as well as can be expected, considering the nature of the substance. From the mean of the best experiments, shown in the following table, we obtain the figure ·480, which, with a possible variation of about 2%, may be considered as the specific heat of caoutchouc :—

Summary of Results.

Caoutchouc.

Expt	W	K	M	$M'\sigma$	T	t	θ	C	x
1.	298·07	6·1	23·94	·65	95 3	15·38	18·28	·12	·471
2.	298·46	6·1	18·82	·68	97·0	14·84	17·25	·16	·486
3.	295·4	5·1	18·35	1·01	98·2	14·32	16·84	·12	·474
4.	293·3	5·1	19·55	·85	98·5	15·01	17·74	·12	·483
5.	250·0	4·0	18·76	·44	98·0	16·35	19·18	·12	·484
6.	298·3	5·7	41·28	·06	99·0	18·72	23·39	·24	·478

Experiments with Oils.

Some preliminary experiments have been made with the oils distilled from caoutchouc. The caoutchouc was distilled in an iron retort, and the vapours condensed; then the liquid was shaken up with sulphuric acid, washed well with water, and re-distilled into different fractions. The lightest fraction—a pale yellow colour—was used, and as the oils are all polymeric, the same results would be obtained from all the fractions. The oils are isomeric with oil of turpentine, whose specific heat is ·46. For calculating the specific heat some fragments of copper were heated and plunged into a known weight of the oil in a small calorimeter, the equation being now as follows:—

$$M\sigma(T-\theta)=(M^1x+k)(\theta-t)$$

and

$$x=\frac{M\sigma(T-\theta)}{M^1(\theta-t)}-\frac{k}{M^1}$$

where x = specific heat of oil.

M = mass of copper.

M^1 = mass of oil.

k = water equivalent of calorimeter and stirrer.

σ = specific heat of the copper.

Temperatures denoted as before.

Example.—65 c.c. oil (sp. gr. = ·93) = 60·45 grm. Copper = 21·63. $T=98{\cdot}0$. $t=18{\cdot}45$. $\theta=23{\cdot}10$; whence by above formula we get

$$x=\cdot464.$$

The results obtained with vulcanised rubber in the form of sulphured cut sheet, were very similar to the pure rubber. There would be about 5% of sulphur present, of which the specific heat is ·202.

Some preliminary experiments made with gutta-percha may also be mentioned. This body, however, is difficult to deal with, as it changes its condition when heated, and again when plunged into the calorimeter, taking a very long time to reach the maximum temperature; gutta-percha contains about 30% of two peculiar resins, to which its physical properties are chiefly due. We propose to give some figures concerning this and some allied substances on a future occasion.

NOTE ON THE PREVIOUS PAPER.

By Arthur Schuster, F.R.S.

WHENEVER the time occupied in a calorimetric experiment is sufficiently long to make a cooling correction necessary, it is usual to reduce the measurements by what is called the Regnault-Pfaundler method, which is sufficiently well known to need no further description. The method is laborious, but it is perhaps the only safe one to adopt. Pape, making certain assumptions regarding the interchange of heat between the hot and cold body, deduces a formula for the cooling correction which is quoted in the foregoing paper. Unfortunately, Pape's investigation involves the integration of a differential equation, and this integration is not correctly performed. It is only an accident that his final result is true as a first approximation. If a second approximation was required, Pape's equations would not give it correctly, and the equation quoted by Messrs. Gee and Terry cannot be taken as right.

It is a matter of some interest to know in how far we may simplify a calorimetric measurement by calculating from theoretical considerations the curve connecting the rise and fall of a thermometer placed in a cold liquid into which a hot body is introduced.

Let

V be the mean temperature of the hot body;

σ_1 the water equivalent of the hot body;

v the temperature of the cold body;

σ_2 the water equivalent of the cold body.

Let t represent the time, and let the calorimeter initially be at the temperature of the enclosure which is taken as zero. Pape

assumes that the passage of heat from the hot body to the cold body is at any time proportional to the difference between their mean temperatures, so that the two following equations would hold:—

$$\frac{dV}{dt} = -\frac{k_1}{\sigma_1}(V - v)$$

$$\frac{dv}{dt} = \frac{k_1}{\sigma_2}(V - v) - \frac{k_2 v}{\sigma_2}$$

where k_1 determines the rate at which heat is interchanged between the hot and cold body, and k_2 determines the loss of heat of the calorimeter to the outside.

The solution of the equations has the form—

$$V = A_1 e^{-\lambda_1 t} + A_2 e^{-\lambda_2 t}$$

$$v = A_1^1 e^{-\lambda_1 t} + A_2^1 e^{-\lambda_2 t}$$

Taking account of the initial conditions, the last equation may be written—

$$v = A\left(e^{-\lambda_2 t} - e^{-\lambda_1 t}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

also

$$k_1 V_0 = A\sigma_2(\lambda_1 - \lambda_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where V_0 is the initial temperature of the hot body.

The two constants λ_1 and λ_2 are connected with k_1 and k_2 in a well-known manner. The two equations (1) and (2) involve four unknown quantities, A, λ_1, λ_2, σ_1, and if A is eliminated between them three observations should be sufficient to determine the specific heat of the hot body.

It will appear that of the two quantities λ_1 and λ_2, one, say λ_2, is small compared to the other, and is determined by the rate of cooling at the end of the experiment, when the temperatures of the hot and cold bodies are nearly alike. If, then, the final cooling correction is determined in the usual way, two unknown quantities remain, and these may be determined by observing the maximum temperature, and the time at which the maximum is reached. The complete solution is thus possible, but it is more convenient to reach the result by making use of the fact that certain quantities are so small that their higher powers are negligible. If v is the maximum temperature, and t' the time at which it is reached, we see from (1) that

$$\lambda_2 e^{-\lambda_2 t'} - \lambda_1 e^{-\lambda_1 t'} = 0$$

hence
$$v = \frac{k_1 V_0}{\sigma_2(\lambda_2 - \lambda_1)}\left(e^{-\lambda_1 t'} - e^{-\lambda_2 t'}\right)$$
$$= \frac{k_1}{\sigma_2}\frac{V_0}{\lambda_1} e^{-\lambda_2 t'}$$

It now becomes necessary to introduce the connection between the two values of k and the two values of λ.

The original differential equations give

$$\lambda_1 + \lambda_2 = \frac{k_1}{\sigma_1} + \frac{k_1 + k_2}{\sigma_2} \quad \ldots\ldots\ldots \quad (3)$$

$$\lambda_1 \lambda_2 = \frac{k_1 k_2}{\sigma_1 \sigma_2} \quad \ldots\ldots\ldots \quad (4)$$

In any actual experiment we should endeavour to make the loss of heat to the outside, which is proportional to k_2, as small as possible, at any rate small compared to k_1, and hence one of the quantities, λ_1 and λ_2, say λ_2, will be small.

As a first approximation, then, we obtain from (3)—

$$\lambda_1 = \frac{k_1}{S}$$

where 1/S is written for $\frac{1}{\sigma_1} + \frac{1}{\sigma_2}$

The complete equation (3) gives

$$\lambda_1 = \frac{k_1}{S} + \frac{k_2}{\sigma_2} - \lambda_2$$
$$= \frac{k_1}{S} + \frac{\lambda_1 \lambda_2 \sigma_1}{k_1} - \lambda_2$$

and hence to the next approximation:—

$$\lambda_1 = \frac{k_1}{S} + \frac{\lambda_2 \sigma_1}{S} - \lambda_2$$

from which it follows that

$$\frac{k_1}{\lambda_1 \sigma_2} = \frac{S}{\sigma_2} + \frac{\lambda_2}{\lambda_1}\frac{S - \sigma_1}{\sigma_2}$$

and hence

$$v = \frac{\sigma_1 V_0}{\sigma_1 + \sigma_2} e^{-\lambda_2 t'}\left(1 - \frac{\lambda_2}{\lambda_1}\frac{\sigma_1}{\sigma_2}\right)$$

If there was no cooling the final temperature would be

$$v + \delta = \frac{\sigma_1 V_0}{\sigma_1 + \sigma_2}$$

where δ represents the correction to be applied to the observed maximum. Hence

$$\delta = \frac{\sigma_1 V_0}{\sigma_1 + \sigma_2}\left(1 - e^{-\lambda_2 t'}\right) + \frac{\lambda_2}{\lambda_1}\frac{\sigma_1}{\sigma_2} v$$

If $\lambda_2 t'$ is small so that higher powers may be neglected, the correction finally becomes—

$$\delta = \bar{v}\lambda_2 t' + \frac{\lambda_2 \sigma_1 \bar{v}}{\lambda_1 \sigma_2} = \bar{v}\lambda_2 t'\left(1 + \frac{\sigma_1}{\sigma_2 \lambda_1 t'}\right) \quad . \quad . \quad . \quad . \quad (6)$$

It remains to be shown how λ_2 and λ_1 may be determined.

The cooling will become steady as soon as $e^{-\lambda_1 t}$ becomes negligible, hence in that case

$$v = Ae^{-\lambda_2 t}$$

and

$$\frac{dv}{dt}\Big/ v = -\lambda_2$$

Hence λ_2 is the cooling at the end of the experiment in one interval of time reduced to one degree difference between the temperature of the enclosure and that of the calorimeter. The first term in the equation for the correction represents therefore the amount of cooling of the calorimeter during the rise to the maximum, calculated on the assumption that the rate of loss of heat is uniform throughout and equal to the loss at the maximum observed temperature. This term is that used by Messrs. Gee and Terry, and is also the first term of Pape's correction. The second term in the experiments recorded was negligible, and we may easily see under what conditions the term is small. If λ_2 has been found by experiment as shown above, and t' is known, we might find λ_1 from the equation, which gives the maximum of temperature, viz.:—

$$\lambda_1 e^{-\lambda_1 t'} = \lambda_2 e^{-\lambda_2 t'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

It is convenient in the first place to establish an approximate value of λ_1, and to use the equation, if necessary, to find a second approximation. During the first few intervals the rise of temperature chiefly depends on λ_1, and we may write (1)

$$v = A(1 - e^{-\lambda_1 t})$$

where A is approximately the maximum rise; hence

$$\lambda_1 t = \frac{\log \bar{v} - \log v}{\log e} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where v is a temperature observed at the time t soon after the introduction of the body. As the rise then may be irregular, it will be safer to use it only as a first approximation. Equation (5) gives

$$\log \frac{\lambda_1}{\lambda_2} = (\lambda_1 - \lambda_2) t' \log e \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If the value of λ_1 obtained by (7) is substituted in the left hand side of this equation, a sufficiently near approximation for the same quantity will be obtained. Thus in the experiment recorded in the previous paper, λ_1, as found from (7), is 0·7; λ_2 is found to be ·0045, and (8) then gives $\lambda_1 = 0{\cdot}6$.

The second term in the correction as given in equation (6) is now found to be negligible, but chiefly because σ_1 is small compared to σ_2. This need not always be the case. If we were to determine the specific heat of a body like paraffin, which becomes viscous at comparatively low temperatures, we should have to take large quantities heated, perhaps, only 10 or 20 degrees above the temperature of the water, and in this case the second term in the cooling correction would have to be taken into account.

If another observation is taken sufficiently soon after the introduction of the hot body to allow the higher powers of $\lambda_1 t$ to be neglected so that the equation

$$v = A\lambda_1 t = \bar{v}\lambda_1 t$$

holds with sufficient approximation, Equation (6) may be written

$$\delta = \bar{v}\lambda_2\left(t' + \frac{\sigma_1}{\sigma_2}\frac{t\bar{v}}{v}\right)$$

where v is an observation of temperature taken at the time t_1.

This is the form in which I gave the equation to Mr. Gee to be used in his reductions, and taking account of the difference in the notation it is identical with that quoted by him.

It is easy to generalise the equations so as to render them applicable to the case that the calorimeter at the beginning of the experiment is not in thermal equilibrium with its surroundings.

ON THE COMPARISON OF THERMOMETERS.

By Thos. Ewan, Ph.D., B.Sc., *and* W. W. Haldane Gee, B.Sc.

(From the Memoirs of the Manch. Lit. and Phil. Society.)

THE experiments described in the following paper were undertaken with the object of finding a practical method for standardising platinum resistance thermometers and comparing them with mercurial thermometers.

The platinum thermometer, as suggested by Siemens, has been improved by Callendar,* who found that, if the ratio

$$100\left(\frac{R_t - R_o}{R_{100} - R_o}\right),$$

be taken as "temperature by platinum thermometer" $=pt$ [where R_t, R_o, and R_{100} are the resistances at $t°$, 0°, and 100° respectively], then the differences between the readings of an air thermometer and those of the platinum thermometer are represented by the equation

$$t - pt = \delta\left\{\left(\frac{t}{100}\right)^2 - \frac{t}{100}\right\}.$$

For the specimen of platinum wire used by Callendar the constant δ was found to be 1·57. This formula agreed with the results within 1 % through a range of 700 degrees.

Griffiths† has confirmed these results, and has shown that the δ formula represents the differences between the readings of air thermometer and the platinum thermometer with even greater accuracy than Callendar had supposed.

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* *Phil. Trans.*, 1887, Pt. A.

† B. A. Reports, Leeds Meeting, 1890. (*Electrician*, Oct., 1890.)
Proc. Roy. Soc., June, 1890.
Callendar and Griffiths, *Proc. Roy. Soc.*, Dec., 1890.
Griffiths, *Phil Trans.*, Pt. A, 1891

Under these circumstances we thought it desirable to elaborate a method which would allow of the platinum thermometer being standardised and then used for comparison with mercury thermometers, and especially to find what degree of accuracy could be attained without the use of elaborate precautions or special apparatus.

To determine the fixed points on the scale of the platinum thermometer we immersed it in the vapour of water boiling under diminished pressure. The same apparatus served for the comparison with the mercury thermometer.

Regnault's tables of the pressures of aqueous vapour have already been used by Shaw* for measuring temperatures. He

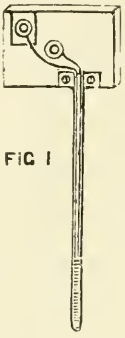

FIG 1

aspirated a known volume of air saturated with moisture at a temperature "t," through tubes filled with pumice moistened with strong sulphuric acid. The increase in the weight of these tubes gave the data necessary for calculating t. This method is, however, only applicable to ordinary temperatures.

The platinum thermometer (Fig. 1.) which we used was made under the direction of Mr. E. H. Griffiths, by Mr. Thomas, of Cambridge. It consists of a platinum wire coiled on a roll of asbestos paper. The ends of this wire are soldered to thick copper leads, which communicate with binding screws. The coil is protected by a thin glass tube closed at the lower end. The copper leads are insulated by narrower glass tubes. The resistance of the coil at 0° was 10·637 ohms.

The mercurial thermometer used was one by Hicks, and was

* *Phil. Trans.* (Cambridge), 1885.

graduated in half degrees. The calibration of the stem gave the following corrections :—

Correction at	100°	+·38
,, ,,	90	+·32
,, ,,	80	+·27
,, ,,	70	+·22
,, ,,	60	+·15
,, ,,	50	+·14
,, ,,	40	+·12
,, ,,	30	+·08
,, ,,	20	+·06
,, ,,	10	+·03
,, ,,	0	+0·0

The measurements of the resistance were made by means of a post-office resistance box, by Elliott Bros., and a sensitive galvanometer. The resistances were read directly on the box to ·01 ohm, and the numbers in the third decimal place obtained by interpolation from the deflections of the galvanometer.

The resistance coils were of German silver, and were correct at 19° C. The temperature was taken by a thermometer (graduated in tenths of a degree) placed inside the box, but owing to the construction of the latter the thermometer could not be in actual contact with the coils, which introduces a considerable uncertainty into the correction for the temperature of the coils. Most of the irregularities in the measurements of temperature by platinum thermometers are probably due to this. The correction was applied by the formula

$$R_{19} = R_t[1 - 0{\cdot}0004433\ (19 - t)]$$

An error of 1° in taking the temperature of the coils may make an error of 0·2° in the temperature measured by the platinum thermometer.

The platinum coil was connected with the resistance coils by thick leads, consisting of bundles of copper wires. Three or four Leclanché cells were used, and a commutator was included in the circuit.

After several unsuccessful attempts the apparatus shown in Fig. 2 for boiling water under diminished pressure was found to give satisfactory results.

It consists of a copper vessel A, such as is used for determining the boiling point of thermometers. The upper end is closed by

an india-rubber stopper, through which two glass tubes pass. One of them terminates shortly below the stopper, and through it the stem of the platinum thermometer passes, the joint being closed air-tight by a piece of india-rubber tubing slipped over both tubes. The other is long enough to admit the mercurial thermometer, and is closed at the lower end, and filled with water covered by a layer of paraffin, or better, with mercury.

It is necessary to protect the mercury thermometer in this way, as the exposure of its bulb to the diminished pressure inside

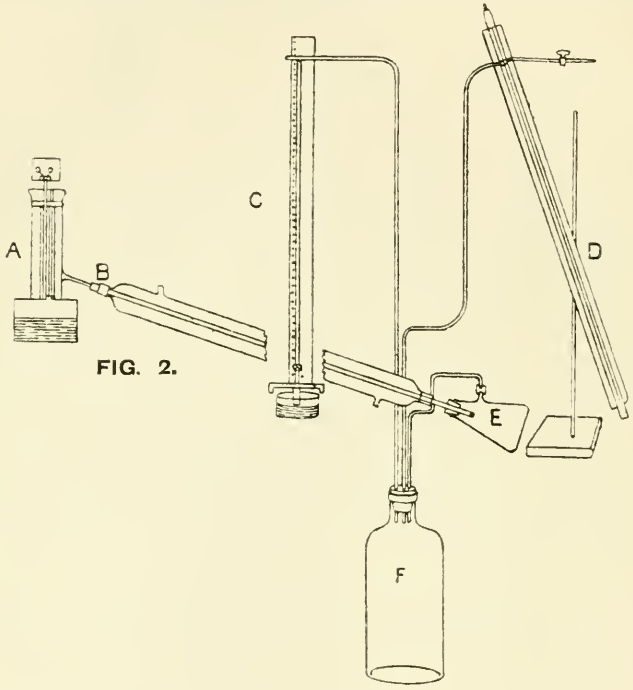

FIG. 2.

the apparatus may produce a very sensible error in its indications. (*Vide Guillaume Thermométrie de Précision.* Paris, 1889.)

Regnault,* in his experiments on the vapour tension of steam, made use of a similar arrangement. Some experiments which he made on this point showed that the readings of the thermometer at 100° were the same whether it was directly exposed to the steam or not.

* *Mèm. de l'acad.*, t. 21.

The steam issuing from the opening C is condensed by an ordinary Liebig's condenser. It is important that there should be no narrow tubes in this part of the apparatus, otherwise the pressure in the boiler may be higher than that indicated on the gauge. The gauge (G) was of the simple barometer form, the tube being 12 mms. internal diameter. The height of the mercury was read on a brass meter scale, placed behind the tube, by a telescope at a distance of about 6ft.

The pressure regulator D was of the form described by Nicol,* and Stadel and Schummann,† and was found to give satisfactory results. The pressure could be kept constant within 0·5 mm. for half an hour at a time.

The pressure regulator, the gauge, and the receiver E communicate with one another through the reservoir F, which consisted of a Winchester quart bottle standing in a large vessel full of water.

The first experiments were made with a glass boiling apparatus, but at temperatures below 100° the indications of the thermometer were 0·1° to 0·2° too high. The boiling point of the platinum thermometer was found practically the same in both the glass and the copper apparatus. The difference at lower temperatures is probably due to the fact that water does not boil regularly in a glass vessel under diminished pressure. This irregular boiling gives rise to sudden alterations in the pressure, and to overheating of the steam.

In making the measurements of temperature by the platinum thermometer, the greatest error was (as has already been mentioned) in the correction for the temperature of the resistance box. To eliminate this as much as possible, we took readings of the resistance at 0° and 100° before each set of observations, and then kept the temperature of the coils as constant as possible while the readings at intermediate temperatures were made.

In determining the zero point, the platinum thermometer was left in the ice for at least an hour, and the current only closed momentarily (the first swing of the galvanometer needle being read), in order to avoid heating the wire.

* Nicol, *Phil. Mag.* (5) xxiii, 389.

† Stadel and Schummann, *Zeitschrift f. Instrumenten Kunde*, 391, 1882.

The current was also reversed in order to eliminate thermal effects. No correction was made for the resistance of the copper leads.

The zero point was found at different times.

Resistance at 0°.	Mean.	Difference from Mean.
10·6388	10·6372	+ ·0016
10·6401		+ ·0029
10·6343		− ·0030
10·6360		− ·0012

The following are the determinations of the resistance at 100° in the order in which they were made, and it is curious that they increase and decrease regularly.

		Mean.	Difference from mean.
In glass apparatus.	14·3369	14·3212	+0·0157
	14·3230		+ ·0018
	14·3149		− ·0063
	14·3168		− ·0044
	14·3183		− ·0029
	14·3225		+ ·0013
		Mean.	
In copper apparatus.	14·3226	14·3202	+ ·0024
	14·3243		+ ·0041
	14·3209		+ ·0007
	14·3176		− ·0026
	14·3154		− ·0048

The ratio R_{100}/R_0 from the experiments in the glass apparatus is 1·3463, from those in the copper apparatus 1·3462. These numbers agree very closely with those obtained by Callendar (1·3464), and by Griffiths (1·3462).

The following numbers will serve to show the degree of accuracy which may be reached in measuring the temperature by platinum thermometer.

pt is temperature by platinum thermometer.

R.T. is the boiling point of water according to Regnault, corresponding to the observed pressure.

Resistance.	*pt.*	Pressure.	R.T.	Pt. Corr.	Diff.
14·0414	92·40	573·73	92·33	92·30	+·03
13·8206	86·47	456·22	86·32	86·29	+·03
	$R_{100} = 14·3209$			$R_o = 10·6395$	
14·1371	95·15	636·79	95·13	95·08	+·05
13·8168	86·45	454·98	86·25	86·26	−·01
13·5516	79·24	339·75	78·92	78·98	−·06
	$R_{100} = 14·3154$			$R_o = 10·6360$	
14·0934	93·78	603·71	93·69	93·68	+·01
14·1178	94·40	619·03	94·36	94·32	+·04
13·8947	88·34	490·59	88·20	88·18	+·02
13·6523	81·76	376·38	81·46	81·53	−·07
	$R_{100} = 14·3243$			$R_o = 10·6395$	

The column Pt. Corr. contains the readings of the platinum thermometer reduced to air thermometer degrees by Callendar's formula, viz. :—

$$t - pt = \delta\left\{\left(\frac{t}{100}\right)^2 - \frac{t}{100}\right\}$$

where δ was 1·57, agreeing with the number found by Callendar and Griffiths.

The following table contains the results of a comparison between the readings of (*a*) the platinum thermometer, (*b*) the mercurial thermometer, (*c*) the number from Regnault's Tables (calculated by Broch, *Trav. Bur. Poids et Més. I*).

a.	*b.*	*c.*	*c*—*b.*	*a*—*b.*	Error by direct calibration.
	100·17	100·55	+·38		+·38
	100·00	100·398	+·398		
95·08	94·83	95·13	+·30	+·25	+·35
92·30	92·00	92·33	+·33	+·30	+·33
86·26	86·00	86·25	+·25	+·26	+·30
78·98	78·67	78·92	+·25	+·31	+·26

These numbers show that as far as the experiments have been carried the method is accurate within 0°·1.

If a greater degree of accuracy be desired, the coils may be kept at a constant temperature by means of a thermostat, which is the method used by Griffiths, or the measurements may be made with a slide meter bridge, the comparison being made with reference to coils immersed in water. It would also be advantageous to increase the resistance of the thermometer.

THE SPECIFIC GRAVITY OF SOLUTIONS OF NAPHTHALENE IN BENZENE.

By Arthur Harden, M.Sc.

THE following determinations were made with the object of ascertaining the behaviour of a typical non-electrolyte dissolved in a liquid other than water.

The method employed was that of Sprengel, as modified by Perkin (*Journ. Chem. Soc.*, 1884, p. 443). The specific gravity tubes employed had capacities of about 14 and 15 c.c., and all the weighings are reduced to vacuo. The solutions were all made up by carefully weighing out the substances into stoppered bottles.

The benzene employed was freed from thiophen by treatment with sulphuric acid, and was then further purified by crystallisation and distillation. Its specific gravity at 20°/20° was 0·89790.

Two determinations with each solution were made, the tube being replaced in the bath and readjusted. The results, which are probably accurate to 0·01 %, are given in the following table:—

	% of Naph.	Specific Gravity (20°/20°).		Mean.
		I.	II.	
	0·000	·87967	·87972	·87970
1	0·595	·88053	·88055	·88054
2	1·975	·88241	·88240	·88241
3	5·073	·88660	·88666	·88663
4	9·448	·89259	·89268	·89264
5	14·814	·90001	·90005	·90003
6	18·744	·90556	·90574	·90565
7	27·170	·91771	·91778	·91775

The saturated solution contains 35·5 % of Naphthalene.

In order to ascertain whether the volume occupied by the naphthalene in these solutions is independent of the concentration, two methods may be employed.

I.—Assuming that the benzene retains its original volume, the volume of the naphthalene may be calculated for each solution and hence its specific gravity obtained. It must be remembered that in this way the experimental error is enormously multiplied, especially in the case of the more dilute solutions. An error of 0·01 % in solution 1, *e.g.*, becomes one of nearly 2 % in the specific gravity of naphthalene deduced from that solution.

The numbers obtained in this way are given below, and only show a variation amounting in all to about 0·9 %.

Solution.		Sp. gr. of Naphthalene.
1	.....	1·0475
2	.....	1·04164
3	.....	1·03998
4	.....	1·03916
5	.....	1·03834
6	.....	1·03845
7	.....	1·03813

II.—The theoretical specific gravity of the various solutions may be calculated by taking that of one of them as the standard, and adding or subtracting benzene until the required concentration is obtained, it being assumed that no contraction or expansion takes place.

In the following table are given the results calculated in this way, taking solutions 6 and 7 as the standards:—

Solution.	Specific gravity.		
	Calculated from		Found by experiment.
	6	7	
1	·88050	·88050	·88054
2	·88236	·88236	·88241
3	·88658	·88656	·88663
4	·89259	·89257	·89264
5	·90008	·90004	·90003
6	....	·90568	·90565
7	·91782	....	·91775

The greatest differences here fall within ·01 %, and the conclusion is therefore justified that when a concentrated solution of naphthalene in benzene is diluted, the volume of the resulting solution does not differ by so much as ·01 % from the sum of the volumes of the original solution and of the benzene added.

ON THE ELECTROLYSIS OF SILVER NITRATE *IN VACUO*.

By Arthur Schuster, F.R.S., *and* Arthur W. Crossley, B.Sc.

(From the Proceedings of the Royal Society.)

THE following investigation was undertaken in order to clear up some minor irregularities which occur when the intensity of an electric current is measured by means of a silver voltameter.

The electrolysis of silver nitrate yields, with moderate precautions, such very consistent results that it seemed of interest to follow up the small apparent deviations from Faraday's laws which are found to exist. One of these irregularities has been noticed by Lord Rayleigh, who found that the deposit of silver from a hot solution was about one part in two thousand heavier than the deposit from a cold solution. A second anomaly lies in a small but regular discrepancy in the deposits when these are taken simultaneously in platinum bowls of different sizes; the difference, according to our experiments, seems to depend on the current density at the *anode*. But the chief part of this paper will deal with the fact discovered by us, that the deposits are slightly larger when the electrolysis is conducted *in vacuo* than when, as usual, the voltameters are exposed to air at the ordinary pressure. This difference we trace to the effects of dissolved oxygen, for when the electrolysis is carried out in an atmosphere of oxygen the deposits are smaller than those obtained in air.

The apparatus we employed to obtain a deposit *in vacuo* is illustrated in Fig. 1. An inverted bell-jar, closed at the bottom by an india-rubber stopper and at the top by a plate of glass, contains a tight-fitting cylindrical cage of wire gauze, which

serves as support to the electrodes. The platinum basin is placed on two stout copper wires, F, which are soldered to the cage. Metallic contact between the wires and the bowl is secured by the help of tinfoil, which is wrapped round the wires and forms a cushion on which the bowl rests. One of the wires leading to the battery is soldered to the cage. The anode is suspended from a glass rod, C, fixed to the cage near its upper end, the current

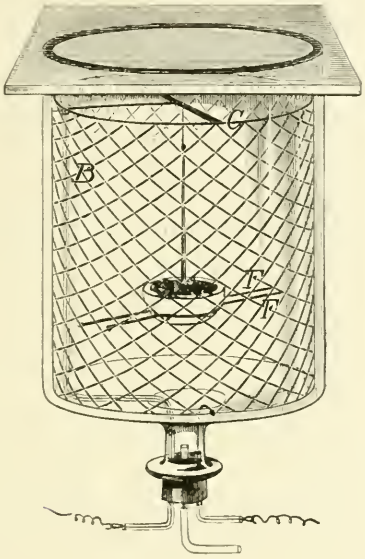

FIG. 1.

being conveyed to the anode by an insulated wire passing through a glass tube, B, which is also secured to the cage. Three pieces of glass tubing pass through the india-rubber stopper; one serves to exhaust the vessel, while the wires leading to the battery pass through the remaining two.

The stopper is rendered airtight by means of Faraday cement, and some grease has to be used to prevent leakage between the glass plate and bell-jar. To prevent particles of this grease contaminating the solution, a tightly-fitting piece of cardboard, not shown in the figure, was placed above the cage. In the latter part of the investigation two nearly identical bell-jars were used.

The same current always passed through two or three voltameters in succession, and the deposits obtained simultaneously were compared with each other. One of the platinum bowls, to

be referred to as the large bowl, has a diameter of 5 inches, while the smaller bowl had a diameter of $3\frac{1}{2}$ inches.

The silver anodes had a thickness of about 2 mms., and generally larger anodes were used in the large bowl than in the small one. With respect to the contact between the anodes and the platinum wires conveying the current, it seems worth while to draw attention to a precaution, which, if neglected, may cause serious trouble. We placed at first, for the sake of convenience, the anodes simply into two loops of platinum wire. These loops crossed at right angles as in Fig. 2. The current under these circumstances is apt to pass partly from the platinum wires, and dark red crystals (probably Ag_2O_2) then shoot out rapidly and form a bridge across the electrolyte.

We have not observed similar effects when the silver plates were perforated, and the platinum wires which passed under the

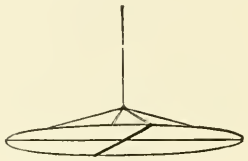

Fig. 2.

silver plate were everywhere in metallic contact with it. We used filter paper to cover the anodes, and followed generally Lord Rayleigh's instructions regarding the conduct of the experiment. The platinum basins were in some experiments first cleaned out with sand, but often this was not done. They were then washed with (1) concentrated nitric acid, (2) strong caustic soda, (3) tap water, (4) distilled water. They were dried roughly with a clean silk handkerchief and heated over a Bunsen flame. After an hour's cooling they were weighed. The deposits of silver were washed three or four times with distilled water, and allowed to stand under water for a night; they were then again washed several times and dried in an air bath at first at 100° C.; the temperature was finally raised to 160° for ten minutes. After an hour's cooling, the final weighings were taken.

In a large number of experiments it almost certainly happens that some anomalous results are obtained, either through insufficient washing or through loss of small quantities of silver. We

give, without exception, the result of each experiment, and think that on the whole they show a remarkable consistency in the indications of the silver voltameters. The effects we investigate are the differences in the deposit of less than one part in a thousand, and the possibility of investigating these differences is a proof that the electrolysis of silver nitrate can safely be trusted to that degree of accuracy.

The only serious source of error against which we had to guard was the prevention of leakage in the leads between the two voltameters.

That our results can in no way be attributed to such leakage is shown by the fact that the voltameters were used in the same position with the bell-jar exhausted or full of air. When the jar was full of air, the difference in the deposit disappeared, except for the small anomaly due to the different sizes of the basins.

When the jar is exhausted, it might be thought that a film of moisture could condense outside the platinum bowl, owing to the cooling due to evaporation in an atmosphere saturated with vapour. If such a film were to a certain extent to short-circuit the bowl, a smaller deposit would be formed *in vacuo;* but our effect is an increase, not a diminution, of the deposit. Our leads were all carefully insulated, and as the resistance of the voltameters was never more than 1 ohm, there is no difficulty in avoiding leakage to the extent required.

For the sake of clearness, we do not give our results in the order in which they were obtained, but the numbers attached to each experiment represent the order in which they were made. We begin by comparing together the deposits obtained in bowls of different sizes, both being in air.

With the exception of the last three observations, the results give a consistent difference of about two parts in ten thousand in favour of the larger bowl. With respect to the last three observations, we have to offer the following explanation: In order to trace, if possible, the difference between the results obtained with large and small bowls, we used in these experiments two anodes of the same size, while in all other cases the anodes were approximately proportional to the size of the bowl. Experiment 12 is anomalous; we cannot account for the difference of 3 milligrams in favour of the small bowl, and simply record the observation;

TABLE I.

Number of experiment.	Date.	Strength of solution in per cent.	Approximate current in ampères.	Duration of electrolysis in minutes.	Weight of deposits.		Difference in mgrms.	Percentage difference.
					Large bowl.	Small bowl.		
4	Jan. 15	12	0·58	34	1·3223	1·3220	+0·3	0·023
7	,, 27	12	0·70	30	1·4229	1·4226	+0·3	0·021
9	Feb. 2	12	0·59	120	4·7616	4·7606	+1·0	0·021
15	March 25	15	0·56	60	2·2364	2·2361	+0·3	0·014
16	,, 31	15	0·55	60	2·2068	2·2060	+0·8	0·036
12	March 17	12	0·78	60	3·1653	3·1686	−3·3	−0·106
13	,, 19	15	0·83	60	3·3518	3·3517	+0·1	0·003
14	,, 23	15	0·55	60	2·2410	2·2410	+0·0	0·000

but do not think that this one experiment can render the results of the others doubtful, especially when taken in conjunction with Lord Rayleigh's observations, presently to be referred to. Experiments 13 and 14 seem to show that when anodes of the same size are used the discrepancy between the bowls disappears. This confirms an impression we have gained that the effect is possibly due to secondary products formed at the anode when the current density there exceeds a certain value. It seems certain that too great a current density at the anode is accompanied by a smaller deposit, but our experiments are not sufficient to decide whether the systematic difference in the two bowls is to be ascribed to the same cause.

TABLE II.—*Comparison of Deposits obtained by Lord Rayleigh in Large and Small Bowls.*

Date.	Deposit in large bowls.	Deposit in small bowls.	Difference in mgrms.	Percentage difference.
	grms.	grms.		
Nov. 29	3·0166	3·0165	+0·1	+0·003
Dec. 4	2·9907	2·9902	+0·5	+0·017
Feb. 18	2·3484	2·3482	+0·2	+0·009
		2·3483	+0·1	+0·004
Feb. 22	3·2977	3·2966	+1·1	+0·033
		3·2979	−0·2	−0·006
Feb. 29	2·2698	2·2693	+0·5	+0·022
		2·2701	−0·3	−0·013
Mar. 5	1·2247	1·2247	±0·0	±0·000
		1·2248	−0·1	−0·001
Mar. 10	1·0648	1·0643	+0·5	+0·047
		1·0645	+0·3	+0·028
Mar. 14	1·2897	1·2892	+0·5	+0·039
		1·2893	+0·4	+0·031
			Mean.....	+0·015

Lord Rayleigh, in his experiments on the silver voltameter, used two bowls of approximately the same size as ours, and the foregoing comparison will show that the difference in the deposits pointed out by us also appears in his results.

In Table II we have entered in two separate columns the deposits obtained by Lord Rayleigh simultaneously from silver nitrate solutions in large and small bowls respectively.

The mean deposit in the large bowls is therefore greater by approximately the same amount as in our experiments. In three cases only were the deposits in the small bowls heavier; and in two out of these three cases the bowl showing these larger deposits contained a 30 per cent. solution, while the other at the same time was filled with a 15 per cent. solution. It seems possible, therefore, that when the strength of the solution is increased to 30 per cent. the difference due to the size of the bowls will disappear. We have recalculated Lord Rayleigh's value for the equivalent of silver, taking the deposits in the large and small bowls separately, using the weight of silver deposited before heating to verge of redness; we find for the equivalent of silver:—

(*a*) calculated from deposits in large bowls..... 0·0111817
(*b*) ,, ,, ,, small ,, ... 0·0111797

Mean..... 0·0111807

The heating to redness seems to affect the deposits equally, and reduces the weight, on the average, by about one part in ten thousand, which accounts for the difference between the above mean and the equivalent as given by Lord Rayleigh and Mrs. Sidgwick.

In some of our later experiments we used three voltameters in series, two of them being kept in an exhausted receiver.

This arrangement allowed us to judge whether the difference in the results obtained with large and small bowls persisted *in vacuo*. The results are not very concordant, but the average deposits are heavier in the large bowl, and hence we do not believe that the influence of current density can be ascribed to the presence of air in the solution.

In Experiment 27 the manipulation differed, in so far as the bowls were cleared out with sand before use: a proceeding adopted in the first experiments as far as the eleventh, but abandoned

TABLE III.—*Pressure about* $1\frac{1}{8}$ *inches.*

Number of experiment.	Date.	Strength of solution in per cent.	Approximate current in ampères.	Duration of electrolysis in minutes.	Weight of deposits.		Difference in mgrms.	Percentage difference.
					Large bowl.	Small bowl.		
18	April 30	20	0·5	60	1·9740	1·9736	+0·4	+0·022
19	May 4	20	0·5	60	2·0239	2·0231	+0·8	+0·040
20	,, 6	20	0·5	60	2·0088	2·0090	−0·2	−0·010
21	,, 8	12	0·5	60	2·0566	2·0562	+0·4	+0·020
22	,, 11	12	0·45	60	1·8785	1·8781	+0·4	+0·021
23	,, 13	12	0·75	40	2·0470	2·0469	+0·1	+0·005
24	,, 20	12	0·75	40	2·0255	2·0252	+0·3	+0·015
25	,, 25	12	0·5	30	1·0117	1·0120	−0·3	−0·030
26	,, 27	12	0·5	30	0·9795	0·9796	−0·1	−0·010
27	,, 29	12	0·5	30	1·0057	1·0039	+1·8	+0·180
			Sum including 27.....		17·0112	17·0076	+3·6	+0·021
			Sum excluding 27.....		16·0055	16·0037	+1·8	+0·011

afterwards. We cannot, of course, draw any conclusions from a single experiment, but it does not seem impossible that the complete removal of the old surface by washing with sand renders the effect of current density more prominent. There is, no doubt, a difference in the condition under which the electrolysis is carried out, according as the deposit takes place on platinum as in the first few seconds, or on silver as in the later stages, and after a number of experiments there may be a thin layer of silver, possibly an alloy of silver and platinum, which resists the action of acid, and can only be scraped out with sand. It is to be noted that Kohlrausch took his silver deposits on platinum which had previously been covered with a layer of silver; while in Lord Rayleigh's experiments the silver deposits were removed from the dish before a new experiment was made. The difference may account for the somewhat greater equivalent found by Kohlrausch; but the concordance of the results shows that there can be no systematic difference amounting to more than a few parts in ten thousand.

We turn now to the main part of the investigation, which is the comparison of the deposits obtained in air and *vacuo*. The solution used in the different voltameters was always taken out of the same bottle. We had intended in this way to make sure that any difference in the deposits was not due to some chemical difference in the solutions. It did not occur to us at the time that the solution in one voltameter being freed of air, we should gradually diminish the amount of air also in the other voltameter, for the solutions were kept in stoppered bottles, which did not allow of a ready re-absorption of oxygen. It will be seen that the differences in the deposits, when these were taken in air and *vacuo*, were larger and more regular in the first experiments than later on, and this may have been due to the gradual elimination of oxygen out of the solution.

Our first experiments were made with the large bowl placed *in vacuo*, and the small one in air. The results, to which a later one is added for the sake of completeness, are embodied in Table IV. Experiment 17 was not a satisfactory one, as will be explained later on, and is therefore included in square brackets.

The large difference between the result obtained in air and *in vacuo* first drew our attention to a possible influence of the size

TABLE IV.—*Comparison of Deposits in Air at Atmospheric Pressure and under a Reduced Pressure of about* $1\frac{1}{2}$ *inches.*

Number of experiment.	Date.	Strength of solution in per cent.	Approximate current in ampères.	Duration of electrolysis in minutes.	Weight of deposits.		Difference in mgrms.	Percentage difference.
					Large bowl *in vacuo*.	Small bowl in air.		
1	Jan. 9	12	0·6	31	1·2468	1·2451	1·7	0·141
3	,, 14	12	0·6	30	1·2005	1·1989	1·6	0·133
17	April 27	20	0·5	60	[2·0183]	[2·0144]	[3·9]	[0·195]

TABLE V.—*Comparison of Deposits in Air at Atmospheric Pressure and under a Reduced Pressure of about* $1\frac{1}{2}$ *inches.*

Number of experiment.	Date	Strength of solution in per cent.	Approximate current in ampères.	Duration of Electrolysis in minutes.	Weight of deposits.		Difference in mgrms.	Percentage difference.
					Small bowl *in vacuo*.	Large bowl in air.		
5	Jan 21	12	0·7	38	1·7255	1·7243	1·2	0·070
6	,, 23	12	0·6	33	1·4361	1·4350	1·1	0·078
8	,, 29	12	0·6	120	5·1036	5·1014	2·2	0·043

TABLE VI.—*Comparison of Deposits in Air at Atmospheric Pressure and under a Reduced Pressure of about* $1\frac{1}{2}$ *inches, the Anode* in vacuo *being small.*

Number of experiment.	Date	Strength of solution in per cent.	Approximate current in ampères.	Duration of electrolysis in minutes.	Weight of deposits.		Difference in mgrms.	Percentage difference.
					Small bowl *in vacuo.*	Large bowl in air.		
10	Feb 5	12	0·6	120	4·8455	4·8477	−2·2	−0·046
11	„ 7	12	0·9	86	5·1829	5·1830	−0·1	−0·000

of the bowl. The experiments made to clear up this point have already been described. A few deposits were taken with the small bowl *in vacuo* and the large bowl in air; although the two effects counteract each other, the deposits *in vacuo* are larger than those in air, as is shown by Table V.

On the supposition that the effect due to the size of the bowl is the same in air as it is *in vacuo*, we may combine the results of Tables IV and V, and thus find that the deposits of silver *in vacuo* are about one part in a thousand larger than those in air. The next two experiments (Table VI) were a surprise.

We traced the cause of the anomalous results shown in this table. The anode of the small bowl had by repeated use been gradually dissolved; the current density was consequently increased. Under these circumstances the current becomes unsteady, polarisation effects make themselves apparent, and the deposits are no longer trustworthy. The deposits taken when the current density is too great have generally a yellow colour. We are reminded of some old experiments in which by increasing the current density black deposits were obtained on the kathode, which at one time were supposed to be a hydride of silver. Poggendorff is generally stated to have proved that the black deposit is not a compound, but silver in a finely divided state. On referring to Poggendorff's paper, his experiments do not seem convincing, and he has expressed himself with more caution than those who quoted him afterwards. He states, however, that the black deposit often suddenly changes into a light one. Some observations made by Mr. Hoskyns Abrahall in the Owens College Laboratory, as well as our own experiments, lead us to believe that it is the current density at the anode more than that at the kathode which introduces the anomalous results. When the deposits are thus untrustworthy, the current, as far as we are able to judge, is always unsteady, so that no danger arises when the silver voltameter is used for the calibration of instruments.

At this stage of the inquiry we introduced a second bell-jar and a second voltameter of approximately the same size as the small one previously used. The balance was also changed, and the weighings were taken on a new short-beam balance. This balance was unsteady in its indications after first setting up, and

TABLE VII.—*Comparison of Deposits in Bowls of the same size, taken under Atmospheric Pressure and a Reduced Pressure.*

Number of experiment.	Date.	Strength of solution in per cent.	Approximate current in ampères.	Duration of electrolysis in minutes.	Pressure in bell-jar in inches.	Weight of deposits.		Difference in mgrms.	Percentage difference.
						In vacuo.	In air.		
17	April 27	20	0·5	60	2	[2·0135] or [2·0150]	[2·0144]	?	?
18	,, 30	20	0·5	60	$1\frac{1}{1}$	1·9736	1·9726	1·0	0·052
19	May 4	20	0·5	60	$1\frac{3}{16}$	2·0231	2·0228	0·3	0·015
20	,, 6	20	0·5	60	$1\frac{1}{1}$	2·0090	2·0085	0·5	0·025
21	,, 8	12	0·5	60	$1\frac{1}{1}$	2·0562	2·0559	0·3	0·015
22	,, 11	12	0·45	60	$1\frac{1}{8}$	1·8781	1·8778	0·3	0·016
23	,, 13	12	0·75	40	$1\frac{1}{8}$	2·0469	2·0470	−0·1	−0·005
24	,, 20	12	0·75	40	$1\frac{1}{8}$	2·0252	2·0248	0·4	0·020
25	,, 25	12	0·5	30	$1\frac{1}{8}$	1·0120	1·0116	0·4	0·040
26	,, 27	12	0·5	30	$1\frac{1}{8}$	0·9796	0·9787	0·9	0·090
27	,, 29	12	0·5	30	$1\frac{1}{8}$	1·0039	1·0037	0·2	0·020
29	Aug. 17	12	0·5	60	$1\frac{1}{8}$	1·8523	1·8495	2·8	0·152
30	,, 19	12	0·5	60	$1\frac{1}{8}$	1·9003	1·8990	1·3	0·070
31	,, 24	12	0·5	60	$1\frac{1}{8}$	1·8999	1·8989	1·0	0·055
							Mean.....		0·043

a sudden change of zero while one of the basins was being weighed renders the result of Experiment 17 doubtful. The numbers obtained in this experiment are therefore included in square brackets in our tables. Table VII gives the comparison of the deposits in air and *in vacuo* taken in basins of nearly the same size. A glance at the numbers can leave no doubt as to the reality of the increase in the deposit under reduced pressure, although the amount of the increase is a little uncertain. There is only one case (Experiment 23) in which the deposits are practically identical, and in that case it was noticed that the deposit *in vacuo* was yellow—an indication that the current density was probably just a little too large. The average difference between the deposits is about one part in two or three thousand.

In the last three experiments, which gave comparatively large differences, the solutions used were kept separate between the experiments, and this leads us to think that we had previously committed an error in mixing our solutions, which, as has already been stated, must gradually have become free of air. Experiment 29 shows, however, too great a difference; some of the silver in the air bowl may have been lost in the washing.

It seems remarkable that the electro-chemical equivalent of silver as deduced from the electrolysis *in vacuo* is almost identical with that obtained in Lord Rayleigh and Mrs. Sidgwick's deposits from hot solutions.

One point as yet remains to be discussed. It was reasonable to assume that the increased deposit *in vacuo* was due to the removal of the oxygen out of the solution. In order to obtain more definite information, we took some deposits in an atmosphere of oxygen. In the first experiment the two bell-jars were exhausted, and one of them filled with oxygen, which was allowed to stand for three hours over the solution before electrolysis.

The result was as follows:—

Deposit in air	(small bowl)	.....	1·8618
,, oxygen	,,	.....	1·8618
,, ,,	(large bowl)	.....	1·8624

There is here no difference except that due to the size of the bowl. As it seemed doubtful whether the oxygen had in the course of three hours been absorbed to its full extent by the

solution, three more experiments were made and conducted as follows :—

One small basin was kept in air as before ; the other was kept *in vacuo*, while the large basin was filled with a solution which after boiling had a stream of oxygen passed through until it was considered that the liquid was saturated with the gas. The solution thus prepared was kept in an atmosphere of oxygen. The comparison between the deposits in air and *vacuo* have already been given (Experiments 29, 30, 31, Table VII).

The weight of the deposits in air and in oxygen was as follows :—

Small bowl in air.	Large bowl in oxygen.	Percentage difference.
1·8495	1·8488	0·04
1·8990	1·8983	0·04
1·8989	1·8981	0·04

We attribute the consistency of these results partly, at any rate, to the fact that the solutions used in the three bowls were kept separate.

In looking at the figures it must be remembered that the large bowl would, if placed in air, have given a larger deposit than the small one, so that the difference between oxygen and air is really greater than would appear from the numbers. There seems little doubt, therefore, that it is the removal of oxygen which is the cause of the increased deposits *in vacuo*.

We have made a number of experiments on the polarisation of the electrodes in our silver voltameters. It does not follow that because there is as much silver dissolved as deposited, there is necessarily complete absence of what is commonly called polarisation. In the first place, the silver is dissolved from a compact sheet which is in a molecular condition different to the crystalline form in which it is deposited. Secondly, the silver is dissolved into a more concentrated solution than that out of which it is deposited, and, as Warburg has pointed out, it is very difficult to distinguish polarisation effects from electro-motive forces due to differences of concentration. Our experiments have shown a small but very consistent polarisation of 0·007 volt, which was the same *in vacuo* and in air.

If, after the polarising current has passed, the anode is taken

out, and replaced after the liquid has been thoroughly stirred, the polarisation is reduced, but still exists to the extent of about one-third the original value. The electro-motive force of polarisation does not seem to be different when the platinum basin is partially or completely covered with silver; but the greater the amount of silver the more slowly does the polarisation die out. We cannot draw any very definite conclusions from these observations, but it seemed worth while to put them on record.

We do not wish to enter into a full discussion of the explanation of our results, but only draw attention to two phenomena investigated by Helmholtz and Warburg respectively. It was shown by Helmholtz that the small current which passes through water under the action of electro-motive forces insufficient to decompose it is due to the presence of dissolved oxygen. If part of the current in a solution of silver nitrate is conveyed by hydrogen atoms, no hydrogen could separate out as gas, but a re-combination with the dissolved oxygen could take place. A small fraction of the current might be conveyed precisely in the way described by Helmholtz. In a subsequent paper,* Helmholtz draws from thermodynamic principles the conclusion that "in very dilute solutions or in acids containing no salts at all, metals, which we otherwise consider unoxidisable in the acid, may dissolve to a small extent with evolution of hydrogen."

Warburg,† in an important paper, shows that voltaic cells may be formed by two pieces of the same metal, dipped into the same solution, if the solution surrounding one of the electrodes contains oxygen in solution. He establishes, further, the fact that in such cases the metal actually enters into solution, and explains thereby a variety of phenomena. From his observations there seems little doubt that even in a solution of silver nitrate, silver may dissolve to a slight extent. The amount so dissolved is possibly increased when the silver is in the nascent state, and may then become measurable.‡

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* *Collected Works*, vol. ii, p. 978.

† *Wiedemann's Annalen*, vol. xxxviii, p. 321.

‡ I have assured myself by experiment that the well-known diminution in weight of copper in copper sulphate does not take place *in vacuo*, care being taken to remove the dissolved oxygen completely. Experiments are at present in progress to investigate the electrolysis of copper *in vacuo*.—A. S

We draw the general conclusion from our experiments that the true electro-chemical equivalent of silver is probably not quite one part in a thousand greater than the value given by Lord Rayleigh, but that, if the experiments are conducted in air and under circumstances similar to those under which Lord Rayleigh's measurements were made, the anomalies described by us do not interfere with the use of the silver voltameter as a current measurer. On the contrary, the fact that we were able to show the existence of systematic differences amounting to not more than two parts in ten thousand is a proof of its trustworthiness.

ON THE ABSORPTION SPECTRA OF SOME COPPER SALTS IN AQUEOUS SOLUTION.

By Thomas Ewan, B.Sc., Ph.D. (*Dalton Chemical Scholar in the Owens College*).

(From the Philosophical Magazine.)

THE following research was undertaken in the hope of throwing some light on the question of the connection between the absorption of light by salts in solution and their molecular structure.

On diluting a solution does a change in its absorption spectrum take place? Whether this is so or not was the first point which I attempted to decide experimentally. A number of researches have already been carried out which bear on this question. The first of these is due to Beer,* who came to the conclusion that a change in the concentration of a solution has the same effect as a corresponding change in the thickness of the layer through which the light passes. The measurements of Bunsen and Roscoe,† and of Zöllner,‡ were in agreement with Beer's law. Melde,§ in 1865, found, by a qualitative method, that the law held good for dilute aqueous solutions of fuchsine; and the greater part of Vierordt's‖ measurements also agree with it.

Lippich,¶ in 1876, observed that the absorption spectrum of

* Beer, *Pogg. Ann.* lxxxvi, p. 78 (1852).

† Bunsen and Roscoe, *Pogg. Ann.* ci, p. 242 (1857).

‡ Zöllner, *Pogg. Ann.* cix, p. 254 (1860).

§ Melde, *Pogg. Ann.* cxxvi, p. 284 (1865).

‖ Vierordt, *Die Anwendung des Spectralapparates*, &c., 1873; *Die Quantitative Spectralanalyse*, &c., 1876.

¶ Lippich, *Wien. Akad. Anz.*, 1876, p. 93.

didymium nitrate is different in strong and in dilute solutions. This was subsequently confirmed by H. Becquerel.*

In 1878 Glan† made a careful series of measurements on aqueous solutions of several salts in different concentrations. He found differences between the absorptions of strong and dilute solutions of about the magnitude of the experimental error.

Settegast,‡ in 1879, found a small decrease in the absorption of solutions of potassium chromate and potassium bichromate, with increasing dilution. This was in agreement with the observations of Glan; while Vierordt (*loc. cit.*), Sabatier,§ and O. Knoblauch‖ found a small increase in the absorption of the more dilute solutions.

O. Hesse¶ (1880) examined alcoholic solutions of cyanine, and obtained numbers which did not agree with Beer's law. His experimental error appears to have been rather large, however; and more recently Ketteler and Pulfrich** have shown that the law holds accurately for such solutions.

The measurements of Pulfrich†† and of Krüss‡‡ on potassium permanganate, and of Marshall§§ and C. Norden‖‖ on carbonyl hæmoglobin and oxyhæmoglobin respectively, show that in these cases the extinction co-efficients are not strictly proportional to the concentrations.

The measurements of B. Walter¶¶ on solutions of fluorescein in ammonia show that Beer's law only holds good up to a certain concentration, above which deviations occur.

Knoblauch,*** finally, was unable to observe any difference between the spectra of strong and dilute solutions of a number of salts which he examined; in a number of other cases differences were observed.

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* Becquerel, *Compt. Rend.* cii, p. 106 (1886).
† Glan, *Wied. Ann.* iii, p. 54 (1878).
‡ Settegast, *Wied. Ann.* vii, p. 242 (1879).
§ Sabatier, *Compt. Rend.* ciii, p. 49 (1886).
‖ Knoblauch, *Wied. Ann.* xliii, p. 738 (1891).
¶ Hesse, *Wied. Ann.* xi, p. 871 (1880).
** Ketteler and Pulfrich, *Wied. Ann.* xv, p. 337 (1882).
†† Pulfrich, *Wied. Ann.* xiv, p. 177 (1881).
‡‡ Krüss, G. and H., *Kolorimetrie u. Quantitative Spectralanalyse*, p. 156 (1891).
§§ J. Marshall, *see* Krüss, *loc. cit.*, p. 211.
‖‖ C. Norden, *see* Krüss, *loc. cit.*, p. 210.
¶¶ B. Walter, *Wied. Ann.* xxxvi, p. 518 (1889).
*** Knoblauch, *Wied. Ann.* xliii, p. 738 (1891).

It would appear, therefore, that the absorption spectrum of a substance in solution is, as a rule, variable to a greater or smaller extent with the concentration. The second question which received attention was the connection between the spectra of the salts of the same acid or base in aqueous solution.

Gladstone,* in 1857, said that "a particular base or acid has the same effect on the rays of light, with whatever it may be combined in aqueous solution." This law, he found, held good generally, though not invariably; and this conclusion was afterwards confirmed by the researches of Bahr and Bunsen,† Bunsen,‡ Landauer,§ Morton and Bolton,‖ Russel and Lapraik,¶ Soret,** Russel,†† Knoblauch, and others.

A discussion of a number of these papers is to be found in a Report on Spectrum Analysis by Dr. Schuster in the British Association Reports, 1882. I will therefore content myself by referring to it. Morton and Bolton found that a large group of double acetates of uranium possess the same absorption spectrum. Knoblauch found in one experiment that the bands of the nitrate and acetate of uranium occupied the same position in dilute solutions, while in stronger solutions they had different positions. The chloride and acetate had the same spectrum. Russel and Lapraik found that the nature of the acid had no influence on the spectrum of uranic salts; while Oeffinger (Dissertation quoted by Knoblauch) apparently found no two salts of uranium with the absorption bands in exactly the same position. The discrepancies are perhaps due to the different observers using solutions of different concentrations.

Knoblauch has shown that, even in the most dilute solutions, the spectra of the copper and potassium salts of eosin are not identical.‡‡

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* Gladstone, *Phil. Mag.* (4) xiv, p. 418 (1857), and *Journ. Chem. Soc.* x, p. 79 (1858).

† Bahr and Bunsen, *Liebig's Ann.* cxxxvii, p. 20 (1866).

‡ Bunsen, *Pogg. Ann.* cxxviii, p. 100 (1866).

§ Landauer, *Berliner Ber.* xi, p. 1772 (1872).

‖ Morton and Bolton, *Chem. News* xxviii, p. 47 (1873).

¶ Russel and Lapraik, *Nature* xxxiv, p. 510 (1886).

** Soret, *Compt. Rend.* lxxxvi, p. 708 (1878).

†† Russel, *Proc. Roy. Soc.* xxxii, p. 258 (1881).

‡‡ Ostwald, *Zeit. Phys. Chem.* ix, p. 588 (1892), was unable to observe the differences which Knoblauch found.

The photometric researches bearing on this question are very few in number. The work of Settegast* and of Sabatier† shows that potassium and ammonium bichromates and chromic acid have very nearly the same absorption spectrum, while that of potassium chromate is quite different.

Erhardt‡ found that the violet solutions of potassium and ammonium chrome-alums and of chromium sulphate have identical absorption spectra, while that of chromic chloride is only very slightly different. The spectra of the other salts of chromium examined were considerably different.

As may be seen from the foregoing historical summary, the experimental material is hardly sufficient to decide whether the absorptions of acid and base in aqueous solution are really independent or not. In strong solutions, speaking generally, they are not; but on dilution changes, greater or smaller, occur, and it is natural to inquire whether there is a limiting dilution beyond which no further change in the absorption occurs, and secondly, supposing that the limit exists, whether the acid and base will exercise their absorptions independently of each other in solutions more dilute than the limit.

To obtain answers to these questions, it was necessary to make photometric measurements of the fraction of the light of each wave-length absorbed by a molecule of different salts of the same metal in solutions of different concentrations. The salts of copper were used, as they seemed to form a suitable material for the measurements.

A preliminary set of measurements was made by a method not unlike that used by Knoblauch,§ but I believe slightly more accurate, owing to the fact that it allows the spectra of the two solutions which are being compared to be seen simultaneously, side by side, in the spectroscope. A short description of it may, therefore, not be out of place.

The spectroscope used was a one-prism graduated arc instrument, by Hilger. The prism had a dispersion from A to H of

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* Settegast, *Wied. Ann.* vii, p. 242 (1879). } *See also* Ostwald, *Zeit. Phys.*
† Sabatier, *Compt. Rend.* ciii, p. 49 (1886). } *Chem.* ii, p. 78 (1888).
‡ Erhardt, Inaugural Dissertation, Freiberg, 1875 (?)
§ These experiments were carried out in January and February, 1891; that is, several months before Knoblauch's paper was published.

about 6° 20′. The solutions were contained in troughs in such a way that a long layer of a dilute solution could be compared with a short layer of a correspondingly strong one. The lengths of the layers and the concentrations of the solutions were always taken inversely proportional to each other; so that the light in both cases passed through the same amount of copper salt. In order that it should also pass through the same amount of water in each case, a long tube full of water was placed in front of the short tube containing the concentrated solution. The diagram, Fig. 1, will make the arrangement sufficiently clear.

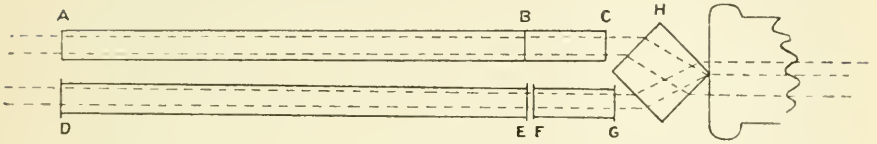

Fig. 1.

A B C is a trough having a movable water-tight partition of glass at B. D E was the compensating tube, full of distilled water; F G the tube destined to contain the concentrated solution. A B and D E were each 888 mms. long, and B C and F G each 102 mms. The light coming from a large Argand burner was rendered approximately parallel by means of a lens. The two bundles of light, after traversing the solutions, pass through the glass cube H, by which means the two spectra are seen, the one above the other, and only separated by a narrow black band due to the edge of the cube, which was not quite sharp. The experiments were carried out as follows: The tubes B C and F G were filled with a strong solution of, say, copper sulphate, and the tubes A B and D E with distilled water. The volumes put into A B and B C were proportional to the lengths of the two parts. The lamp was then arranged so that the two spectra appeared equally bright, and as nearly as possible the same in every respect; measurements of both were then made. The movable partition at B was then removed, the solution in B C mixed with the water in A B, the partition replaced, and measurements made again of the spectrum. By this means any change due to dilution which occurred would be detected. The absorption of the copper salts examined consists of a strong general absorption in the red,

and a greater or smaller absorption in the violet and blue. The readings were made by means of a vertical fibre of silk in the eyepiece of the observing telescope. The positions of the extreme ends of the luminous spectrum were read, and also the positions in which the silk fibre was just visible against the luminous background of the spectrum. The spaces between these readings were taken as the penumbra. The measurements made on the divided arc of the spectroscope were reduced to wave-lengths by interpolation in a curve constructed from measurements of various known lines, which were repeated from time to time.

The following table contains the numbers obtained for copper chloride. Under λ_1 are the wave-lengths of the two positions read for concentrated solutions; under λ_2 the same readings for dilute solutions. The dilute solutions were about one-tenth the concentration of the strong solutions. The numbers are all the means of two or three readings, and the concentrations are given in gram-equivalents of salt in 1 litre of solution. The differences are taken so that a positive difference means an increase in the length of the visible spectrum, and *vice versâ*.

TABLE I.—*Copper Chloride.*

Concentration of strong solutions.	Violet end.			Red end.		
	λ_1.	λ_2.	$\lambda_1-\lambda_2$.	λ_1.	λ_2.	$\lambda_2-\lambda_1$.
4·261	478·7	429·6	+49·1	528·4	531·2	+2·8
	486·8	443·0	+43·8	543·2	540·8	−2·4
2·1305	451·0	439·0	+12·0	537·2	539·6	+2·4
	463·0	451·0	+12·0	551·6	552·4	+0·8
1·7044	431·0	427·6	+ 3·4	572·0	567·8	−4·2
	444·6	437·2	+ 7·4	576·4	579·4	+3·0
1·3612	426·2	421·0	+ 5·2	575·2	575·0	−0·2
	435·8	428·0	+ 7·8	579·8	577·4	−2·4
1·227	424·0	415·4	+ 8·6	580·6	580·6	±0
	430·6	427·0	+ 3·6	584·0	584·0	∓0
1·018	414·8	412·4	+ 2·4	596·6	596·6	±0
	420·8	417·8	+ 3·0	602·0	602·0	∓0

The temperature varied from 15° to 17°·2 on different days. The wave-length of the extreme violet end of the spectrum when

the trough was filled with distilled water was found (on different days) 416·0, 417·2, and 411·2. This shows that the more dilute solutions transmitted the whole of the violet light. The average difference of a single reading from the mean was about ±1·5 units in the wave-length.

The above numbers show that the position of the absorption at the red end of the spectrum does not vary with dilution. The differences vary irregularly in sign, and are of about the magnitude of the experimental error. The absorption in the violet (which extends into the green in the case of the strongest solution) disappears on dilution, so that a layer of 102 mms. of a solution containing about 1 gram-equivalent of salt in a litre shows no noticeable absorption. No change can, of course, be seen on further dilution; it would, however, be rash to conclude that the change has reached a limit at a dilution of 1 gram-equivalent in a litre, as with an Argand burner the visible spectrum only extends to about half-way between G and H; it probably goes on till much greater dilutions are reached, only in the ultra-violet.

TABLE II.

Concentration of strong solution.	Violet end.			Red end.		
	λ_1.	λ_2.	$\lambda_1-\lambda_2$.	λ_1.	λ_2.	$\lambda_2-\lambda_1$.
$CuSO_4$.						
1·89	419·2 428·0	419·2 427·4	±0·0 +0·6	557·0 568·4	557·3 568·4	+0·3 ±0·0
$Cu(NO_3)_2$.						
4·4323	429·0 440·2	429·7 438·3	−0·7 +1·9	525·7 527·8	525·7 527·8	0·0 0·0

The concentration appears to have no influence on the spectra of copper sulphate and nitrate. This agrees with the results of Knoblauch; but, as will be seen later, this is not quite accurate, the concentration really exerting a small influence on the spectra.

Comparisons of the absorptions of $CuCl_2$ and $Cu(NO_3)_2$ in

tolerably dilute solutions showed that no appreciable difference exists between them. The numbers obtained are given in Table III (p. 105).

This method of merely comparing the limits of the spectra of two solutions does not appear to be sufficiently accurate. It is quite possible that general absorptions may exist in a spectrum which, not being sufficiently large to altogether extinguish the light at any place, may pass unnoticed. For example, the photometric measurements made on a strong solution of copper nitrate showed that it exerts a small general absorption over the violet part of the spectrum. This entirely escaped detection by the method described.

According to B. Walter,* the width of the penumbra round an absorption band is connected closely with the presence of more complex molecular aggregates in the solution. On diluting a strong solution of copper chloride, he found a sudden change, at a certain point, in the width of the penumbra, due to the breaking-up of the complex molecules. Table IV (p. 105) contains the measurements of the breadth of the penumbra, calculated from Table I, for a number of solutions of copper chloride.

On the whole the numbers cannot be regarded as showing any sudden diminution in the breadth of the penumbra. The variations appear to be accidental, and are probably due to variations in the brightness of the spectra caused by alterations in the relative positions of the lamp and the tubes containing the solutions.

Photometric Results.

The method of Vierordt was employed, the instrument used being a universal spectro-photometer by A. Krüss of Hamburg. As this instrument has already been described elsewhere,† no lengthy description of it will be necessary. The apparatus consists of an ordinary spectroscrope, the slit of which is divided into two halves, each of which opens symmetrically, and in an accurately measurable manner, by means of micrometer screws, the heads of which carry circles divided into 100 parts. By this

* B. Walter, *Wied. Ann.* xxxvi, p. 523 (1889). Compare Böhlendorff, *Wied. Ann.* xliii, p. 784 (1891).

† *Berichte* xix, p. 2739 (1886); *Zeitschrift anal. Chem.* xxi, p. 182 (1882); G. & H. Krüss, *Kolorimetrie*, p. 90 *et seq.*

TABLE III.

Concentrations.		Length of layer.		Violet end.			Red end.		
$Cu(NO_3)_2$.	$CuCl_2$.	$Cu(NO_3)_2$.	$CuCl_2$.	$\lambda_1 CuCl_2$.	$\lambda_2 Cu(NO_3)_2$.	$\lambda_1 - \lambda_2$.	$\lambda_1(CuCl_2)$.	$\lambda_2 Cu(NO_3)_2$.	$\lambda_2 - \lambda_1$.
1·018	0·1048	102 mm.	990 mm.	413·6 417·6	409·7 414·0	+3·9 +3·6	597·6 603·7	597·6 603·7	±0·0 0·0
0·814	0·814	102 ,,	102 ,,	413·6 —	413·8 —	−0·2 —	596·0 605·4	596·0 605·4	±0·0 0·0
0·814	0·0838	102 ,,	990 ,,	412·1 —	412·8 —	−0·7 —	596·7 602·0	594·3 602·0	−2·4 ±0·0

TABLE IV.

Concentrations	4·261.	2·1305.	1·7044.	1·36.	1·23.	1·02.	0·44.	0·22.	0·176.	0·140.	0·126.	0·105.
Breadth at Red end ..	14·8	14·4	4·1	4·8	4·6	5·4	8·6	12·8	11·6	2·1	3·4	6·4
Breadth at Violet end.	8·1	12·0	13·6	9·6	14·6	6·0	11·4	12·0	9·6	7·0	11·6	5·1

means it is possible to vary the brightness of the upper and lower halves of the spectrum independently of each other by varying the width of the slits. A second slit in the eyepiece of the observing telescope makes it possible to cut out a band in any part of the spectrum. The position of the centre and of the edges of this slit (which also opens symmetrically) can be read off by means of micrometer screws.

The ocular slit was opened 56 divisions (on its screw), which corresponds to a breadth of about 0·27 mm. This divided the whole length of the visible spectrum into 19 parts, in each of which measurements were made.

For an account of the precautions which must be taken in using the instrument, it will be sufficient to refer to the works of G. and H. Krüss and of Vierordt, more especially *Die Anwendung des Spectralapparates zur Photometrie der Absorptions-spectren* (Tübingen, 1873).

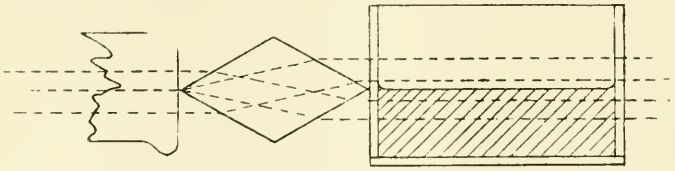

Fig. 2.

The solutions were contained in cells of various lengths. As the measurements are most accurate when the absorption lies between 50 and 85 per cent. of the total light, the length of layer was chosen so that the absorptions to be measured should as often as possible fall between these limits. Three cells were used—viz., a Schulz cell, the glass tube of which had a thickness of 1·006 cm., and two troughs, 7·64 and 22·86 cms. long respectively. When using these troughs the liquid only filled the lower half, the meniscus being placed at the level of the division between the two halves of the double slit. As, however, this produces a black band, about 2 mms. broad, between the two spectra, thereby greatly increasing the difficulty of comparing their brightness, a flint glass rhomb was placed between the trough and the slit, in the same way as in Hüfner's spectro-photometer.* The arrangement is shown in Fig. 2.

* *Zeit. Phys. Chem.* iii, p. 562 (1889).

The ends of the trough were provided with screens of blackened card of sufficient width to prevent reflections from the sides of the trough or from the meniscus. The source of light was, as before, the Argand burner. The measurements were made in a dark room, and extraneous light shut off from the apparatus as much as possible by screens, and from the eye of the observer by a piece of black velvet which covered the eyepiece of the observing telescope. The light from the Argand burner was concentrated by means of two lenses on a hole, about $\frac{1}{16}$ inch diameter, in a black screen, and after passing this was made parallel by a lens of about 15 inches focal distance. The light thus obtained was rather faint, but it was not found possible to obtain reliable results otherwise. The salts examined were carefully purified, and the solutions made with twice distilled water. They were filtered immediately before being examined through fine Swedish filter paper. All the solutions were analysed after being filtered, as the filtration made a small difference in the concentration. The analyses were made by the very convenient method—titration, with thiosulphate solution, after adding excess of potassium iodide—described by Westmoreland.* The concentrations are, as before, given in gram equivalents in one litre of solution.

The measurements are made as follows: The cell, either empty or filled with distilled water, is adjusted before the slit of the spectroscope on a suitable stand, and the ratio of the intensities of the light which has passed through the upper and lower halves of the trough is read, in various parts of the spectrum. This gives the correction to be applied on account of the apparatus. The solution is now placed in the trough, and readings made through as much of the spectrum as possible. Ten or more single readings were made in each region and the mean taken.

The formulæ which I have used in reducing the results are: (1) for the Schulz cell,

$$(1-p)=\frac{b(1-\beta''')^2}{(1-\beta')^2 \cdot a}.$$

(2) For the ordinary troughs,

$$(1-p)=\frac{b(1-\beta)^2}{(1-\beta'')^2(1-p') \cdot a};$$

* *Journ. Soc. Chem. Ind.*, p. 48 (1886).

where $a = \frac{\text{width of lower slit}}{\text{width of upper slit}}$, the two spectra having been made of equal brightness, and the empty trough being before the slit.

b is the same ratio when the trough contains the solution.

p the fraction of the incident light absorbed by the dissolved substance.

p' = the fraction absorbed by the water.

β = loss by reflection at surface between ends of trough and air.

β' = loss by reflection at surface between Schulz cube and air.

β'' = loss by reflection at surface between ends of trough and solution.

β''' = loss by reflection at surface between Schulz cube and solution.

The loss of light due to the absorption of the water was calculated from the numbers of Hüfner and Albrecht.* The following table contains the numbers which were used in reducing the results :—

TABLE V.

Region in Spectrum.	ϵ.	$(1-p')$ for 7·64 cms.	$(1-p')$ for 22·87 cms.
λ 627·7—λ 599·4	0·00108	0·981	....
599·4— 574·2	0·00073	0·987	....
574·2— 551·6	0·00039	0·993	0·980
551·6— 534·1	0·00026	0·996	0·986
534·1— 518·2	0·00019	0·997	0·990
518·2— 502·3	0·00018	0·997	0·990
502·3— 488·3	0·00017	0·998	0·991
488·3— 474·6	0·00016	....	0·992
474·6— 462·8	0·00015	....	0·993

The quantity $(1-p)$ is the fraction of the incident light which has escaped being absorbed by the dissolved substance, and is dependent on the length of layer and concentration of solution. In order to obtain comparable numbers, the extinction-coefficients

* *Wied. Ann.* xlii, p. 1 (1891).

and absorption ratios have been calculated from the values of $(1-p)$. A few words on the connection of these quantities with one another are perhaps not altogether superfluous.

According to Lambert's law we have

$$I' = I\alpha^n, \quad \ldots \ldots \ldots \quad (1)$$

where I' is the light transmitted by a layer of thickness n, of a substance the co-efficient of transmission of which is α. I is the original intensity of the light.

Bunsen and Roscoe* define the extinction-coefficient as the reciprocal of that length of layer of a solution which will reduce the intensity of light by absorption to $\frac{1}{10}$ of its original value.

Substituting, therefore, in equation (1), $I' = \frac{1}{10}$, $I = 1$, and $n = \frac{1}{\epsilon}$, we get

$$\frac{1}{10} = \alpha^{\frac{1}{\epsilon}},$$

or

$$\epsilon = -\log \alpha. \quad \ldots \ldots \ldots \quad (2)$$

From equation (1) we have also

$$-n \log \alpha = \log I - \log I'.$$

Substituting the value of $-\log \alpha$ and putting $I = 1$, we get

$$\epsilon = -\frac{\log I'}{n}.$$

I' is the quantity which before has been called $(1-p)$.

Further, according to Beer's law, if there are two solutions of the same substance, of concentrations c and c', and in lengths of layer l and l', such that

$$cl = c'l', \quad \ldots \ldots \ldots \quad (1)$$

they will absorb the same fraction of the light which passes through them.

Suppose they both transmit the fraction I', then

$$\epsilon = -\frac{\log I'}{l} \text{ and } \epsilon' = -\frac{\log I'}{l'}, \quad \ldots \ldots \quad (2)$$

ϵ and ϵ' being the extinction-coefficients of the two solutions. From (1) we find

$$-\frac{cl}{\log I'} = -\frac{c'l'}{\log I'}; \quad \ldots \ldots \ldots \quad (3)$$

and from (2) and (3), finally, we have

$$\frac{c}{\epsilon} = \frac{c'}{\epsilon'}.$$

That is, the concentration is proportional to the extinction-

* *Pogg. Ann.* ci, p. 235 (1857).

coefficient, and $\frac{c}{\epsilon} = A$. A is, if Beer's law is true, a constant only dependent on the wave-length of the light and on the nature of the substance. The quantity A is called by Vierordt the absorption ratio (*Absorptions verhältniss*).

The following example will make the method of reducing the results clear :—

Solution of $CuCl_2$, concentration = 2·113 gr. eq. in 1 litre.

Trough 7·64 cms. long.

The apparatus correction a was found 1·003, as a mean of 25 readings in various positions in the spectrum.

The following readings were taken with the solution in the trough, in the region between λ518·2 and λ502·3.

Breadth of upper slit.	Lower slit. Upper slit. (b)	Number of Readings.	Greatest difference between two Readings.	Mean. (b)
140	·484	5	3·8	0·485
100	·487	5	2·3	

The refractive index of the ends of the trough was 1·526.

,, ,, of the solution was . . 1·362.

β and β'' are calculated by Fresnel's formula—$\left(\frac{n-1}{n+1}\right)^2$, which gives $\beta = 0{\cdot}0433$ and $\beta'' = 0{\cdot}00325$. The fraction of light transmitted by 7·64 cms. of water is taken from Table V. Putting these values into the expression given for the ordinary troughs, we get

$$(1-p) = \frac{0{\cdot}485 \times (1-0{\cdot}0433)^2}{(1-{\cdot}00325)^2 \times 0{\cdot}997 \times 1{\cdot}003} = 0{\cdot}4473.$$

As

$$\epsilon = -\frac{\log (1-p)}{l},$$

where l = length of layer,

$$l\epsilon = -\log (1-p) = 0{\cdot}34944.$$

Again

$$A = \frac{c}{\epsilon} = \frac{cl}{\epsilon l};$$

$$\log A = \log c + \log l - \log \epsilon l = \log (2{\cdot}113) + \log (7{\cdot}64) - \log (0{\cdot}34944);$$

c = concentration in gram equivalents in 1 litre of solution. On calculating out the above expression,

$$A = 46{\cdot}2.$$

Probable Error.

As there is no reason why the error should be greater in one set of measurements than in another (the measurements being all of the same kind), I have only calculated it for one set of numbers, obtained with a solution of copper chloride containing 2·113 equiv. in 1 litre. The probable error was calculated by the formula $\pm 0{\cdot}6745\sqrt{\frac{S}{n(n-1)}}$. The results are contained in Table VI.

Table VI.

Region in Spectrum.	Number of Readings.	$(1-p)$.	Y.	Z.
551·6—534·1	15	0·083	±0·0014	±3·5
534·1—518·2	15	0·2599	·0016	1·3
518·2—502·3	10	0·4855	·00289	1·3
502·3—488·3	15	0·7020	·00371	1·1
488·3—474·6	15	0·7972	·00469	1·3
474·6—462·8	10	0·7076	·00616	1·7
462·8—452·2	10	0·6125	·00410	1·5
452·2—443·1	10	0·3893	·00676	3·5
443·1—434·2	5	0·1890	·00334	3·7

The final value of $(1-p)$ is calculated from two photometric measurements of the same kind; one, the correction for the apparatus, the other the measurement of the light which passes through the solution. These will both be subject to an error of the magnitude given in column Y. The probable error of the final result will therefore be double this amount. The numbers in column Z represent this final error, calculated as percentages of $(1-p)$. The large error in the violet is due to the small intensity of the light used in that part of the spectrum, and also to the fact that the eye is less sensitive to differences in the intensity of light in the violet than in the middle of the spectrum. At the red end of the spectrum a special error makes itself felt. The measurements are only theoretically accurate, when the part of the curve representing the intensity of the light in the part of the spectrum in which they are made may be considered as a horizontal line. When the absorption curve of the substance

under examination rises or falls rapidly this is no longer the case, and for this reason the measurements on the copper salts in the red end of the spectrum are less accurate than in other parts.

My first measurements on the absorptions by copper sulphate showed a lack of agreement between the numbers obtained with the same solution when different lengths of layer were used. This was found to be due to the light not being parallel, as the differences disappeared when parallel light was used. Something similar appears to have been observed by other investigators. Vierordt* found (with a lamp 15 cms. from the slit, and distilled water in the trough) the ratio of the intensity of the light which had passed through the empty half of the trough to that which had passed through the water to be 0·8; the calculated number is 0·936. Krüss† found the ratio in a Schulz cell 0·905, that calculated being 0·993. I also found the ratio in a Schulz cell 0·91, when the light was not parallel.

The cause of these differences may be found in the fact that placing a layer of a medium with a greater refractive index than air in the path of the light has the same effect as bringing the light nearer to the slit through a distance which is given by the formula $l\left(\frac{\mu-1}{\mu}\right)$, where l is the thickness of the layer of the medium, and μ its refractive index. It must also be remembered that, so long as the collimator is filled with light, an alteration in the distance of the lamp makes no difference in the intensity of the light in the spectrum. The distance of the lamp must therefore be measured from the point at which the collimator just ceases to be filled with light. A comparison with a set of measurements made with pure water showed that at least a considerable part of the difference observed is to be explained in this way.

The following tables contain a number of measurements which were made with parallel light and distilled water in the troughs. The good agreement found between the calculated and observed numbers shows that the loss of light due to dust in the liquids cannot have been very great. I is the ratio of the intensities of the light after passing through the upper and lower halves of the trough.

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* *Anwendung*, &c., pp. 5 and 24. † *Kolorimetrie*, p. 153.

TABLE VII.

Region in Spectrum.	I (found).	I (calculated).	Difference.
SCHULZ CELL.			
λ 599·4—λ 574·2	0·985	0·987	+0·002
551·6— 534·1	0·991	0·985	−0·006
SCHULZ CELL.			
λ 627·7—λ 599·4	0·983	0·987	+0·004
599·4— 574·2	0·979	0·987	+0·008
574·2— 551·6	0·982	0·986	+0·004
551·6— 534·1	0·985	0·985	±0·000
518·2— 502·3	0·988	0·985	−0·003
LAYER OF WATER, 7·64 CMS.			
λ 627·7—λ 599·4	0·949	0·941	−0·008
599·4— 574·2	0·939	0·935	−0·004
574·2— 551·6	0·948	0·929	−0·019
551·6— 534·1	0·935	0·927	−0·008
534·1— 518·2	0·926	0·926	±0·000
502·3— 488·3	0·909	0·926	+0·017
488·3— 474·6	0·919	0·926	+0·007
LAYER OF WATER, 22·87 CMS.			
λ 534·1—λ 518·2	0·927	0·934	+0·007
502·3— 488·3	0·925	0·933	+0·008
474·6— 462·8	0·917	0·931	+0·014

The effect of dust would be to make the observed numbers higher than those calculated. This is sometimes the case, sometimes the reverse.

Table VIII contains the details of the measurements made on the solutions of copper salts.

Under c are found the concentrations of the solutions, in gram equivalents of salt in 1 litre of solution; under l the length of layer in cms.; ϵ is the extinction-coefficient, and A the absorption ratio.

Table VIII.

c.	l.	Region in Spectrum.	$(1-p)$.	$l \cdot \epsilon$.	A.
		Copper Sulphate.			
		λ λ			
2·0324	1·006	627·7—599·4	0·083	1·08096	1·89
		599·4—574·2	0·2944	0·53102	3·85
		574·2—551·6	0·4930	0·30714	6·66
		551·6—534·1	0·6985	0·15582	13·12
		534·1—518·2	0·8171	0·08774	23·25
2·0324	7·64	551·6—534·1	0·0611	1·21424	12·79
		534·1—518·2	0·2220	0·65357	23·76
		518·2—502·3	0·4454	0·35130	44·20
		502·3—488·3	0·6716	0·17286	89·8
2·3803	22·87	518·2—502·3	0·0697	1·15643	47·07
		502·3—488·3	0·2490	0·60386	90·15
		488·3—474·6	0·5021	0·29925	181·9
		474·6—462·8	0·6734	0·17176	316·9
		462·8—452·2	0·7723	0·11220	485·2
		452·2—443·1	0·8103	0·09137	595·8
		443·1—434·2	0·7873	0·10384	523·0
		434·2—427·0	0·7846	0·10535	516·7
0·2856	7·64	627·7—599·4	0·0614	1·21468	1·796
		599·4—574·2	0·2290	0·64017	3·408
		574·2—551·6	0·4700	0·32791	6·654
		551·6—534·1	0·6880	0·16242	13·43
0·2842	22·87	574·2—551·6	0·1077	0·96793	6·715
		551·6—534·1	0·2930	0·53305	12·19
		534·1—518·2	0·5086	0·29361	22·14
		518·2—502·3	0·6884	0·16216	40·08
		502·3—488·3	0·8377	0·07690	84·52
		Copper Chloride.			
4·211	1·006	599·4—574·2	0·0799	1·09711	3·86
		574·2—551·6	0·2403	0·61918	6·84
		551·6—534·1	0·4971	0·30355	13·95
		534·1—518·2	0·6987	0·15573	27·20
		518·2—502·3	0·8339	0·07888	53·70
		502·3—488·3	0·8764	0·05731	73·92
		488·3—474·6	0·7981	0·09797	43·24
		474·6—462·8	0·6591	0·18109	23·39
		462·8—452·2	0·4131	0·38395	11·03
		452·2—443·1	0·2104	0·67687	6·26

TABLE VIII (*continued*).

COPPER CHLORIDE (*continued*).					
c.	*l.*	Region in Spectrum.	$(1-p)$.	$l.\epsilon$.	A.
		λ λ			
2·113	1·006	627·7—599·4	0·0787	1·10406	1·92
		599·4—574·2	0·2536	0·59594	3·57
		574·2—551·6	0·4832	0·31587	6·73
		551·6—534·1	0·6854	0·16405	12·96
		534·1—518·2	0·8187	0·08687	24·47
		434·2—427·0	0·7064	0·15091	14·09
2·113	7·64	551·6—534·1	0·0765	1·11612	14·46
		534·1—518·2	0·2394	0·62092	26·00
		518·2—502·3	0·4473	0·34944	46·20
		502·3—488·3	0·6467	0·18929	85·26
		488·3—474·6	0·7344	0·13406	120·4
		474·6—462·8	0·7064	0·15093	107·0
		462·8—452·2	0·5637	0·24896	64·99
		452·2—443·1	0·3583	0·44579	36·20
		443·1—434·2	0·1739	0·75961	21·25
2·117	1·006	627·7—599·4	0·0662	1·17904	1·81
		599·4—574·2	0·2495	0·60289	3·53
		574·2—551·6	0·4772	0·32131	6·63
		551·6—534·1	0·6796	0·16775	12·70
		434·2—427·0	0·7029	0·15313	13·91
0·4189	7·64	627·7—599·4	0·0216	1·66493	1·92
		599·4—574·2	0·1395	0·85558	3·74
		574·2—551·6	0·3428	0·46496	6·88
		551·6—534·1	0·5665	0·24678	12·97
0·4189	22·87	551·6—534·1	0·1931	0·71418	13·41
		534·1—518·2	0·3996	0·39833	23·99
		518·2—502·3	0·5962	0·22460	42·69
		502·3—488·3	0·7533	0·12303	77·87
		488·3—474·6	0·8495	0·07084	135·2
COPPER NITRATE.					
4·51	1·00	574·2—551·6	0·159	0·79398	5·68*
		551·6—534·1	0·401	0·39449	11·46*
3·9916	7·61	534·1—518·2	0·04011	1·39671	21·83
		518·2—502·3	0·1560	0·80675	37·80
		502·3—488·3	0·3535	0·45165	67·52
		488·3—474·6	0·5184	0·28532	106·9
		474·6—462·8	0·6373	0·19569	155·8
		462·8—452·2	0·6591	0·18106	168·4
		452·2—443·1	0·6782	0·16867	180·8
		443·1—434·2	0·6458	0·18992	160·6
		434·2—427·0	0·6125	0·21289	143·2
0·3552	7·64	627·7—599·4	0·0415	1·38174	1·96
		599·4—574·2	0·1907	0·71958	3·77
		574·2—551·6	0·3588	0·44515	6·09
		551·6—534·1	0·5824	0·23480	11·55
0·3552	22·87	551·6—534·1	0·2218	0·65405	12·42
		534·1—518·2	0·3616	0·34477	23·56
		518·2—502·3	0·6669	0·17593	46·17
		502·3—488·3	0·8208	0·08576	92·57

* These numbers were obtained with light which was not parallel.

The refractive indices of the solutions were determined for sodium light as follows:—

Substance.	Concentration.	Refractive Index.
$CuSO_4$	2·1	1·365
,, ...	0·28	1·336
$CuCl_2$	4·2	1·388
,, ...	2·1	1·362

Table IX contains the absorption ratios of all the solutions examined. The absorption ratio for any substance in solutions of different concentration can be regarded as constant when the differences of concentration are small. The mean, therefore, of the numbers obtained with the solutions of nearly the same concentration has been taken.

TABLE IX.

Position in Spectrum.	$CuSO_4$.		$CuCl_2$.			$Cu(NO_3)_2$.	
	2 eq.	0·28 eq.	4 eq.	2 eq.	0·4 eq.	4 eq.	0·35 eq.
λ λ							
627·7—599·4	1·89	1·79	....	1·86	1·92	....	1·96
599·4—574·2	3·85	3·41	3·86	3·55	3·74	....	3·77
574·2—551·6	6·66	6·81	6·84	6·68	6·88	5·68	6·09
551·6—534·1	12·95	12·65	13·95	13·41	13·19	11·46	11·99
534·1—518·2	23·51	22·05	27·20	25·23	23·99	21·83	23·56
518·2—502·3	45·63	40·45	53·70	46·20	42·69	37·80	46·17
502·3—488·3	89·97	82·73	73·92	85·26	77·87	67·52	92·57
488·3—474·6	181·9	143·2	43·24	120·4	135·2	106·9	....
474·6—462·8	316·9	....	23·39	107·0	....	155·8	....
462·8—452·2	485·2	....	11·03	64·99	....	168·4	....
452·2—443·1	595·8	....	6·26	36·20	....	180·8	....
443·1—434·2	523·0	....	....	21·25	....	160·6	....
434·2—427·0	516·7	....	....	14·00	....	143·2	....

The absorption spectrum of copper sulphate has already been measured by Glan*. He has given his results in the form of fractions of light transmitted—the quantity which I have called $(1-p)$. The light, in Glan's experiments, passed vertically upwards through a glass trough, in the lower part of which was a layer of strong copper sulphate solution, and floating upon this a layer of distilled water. The fraction of the light transmitted was measured, the water and solution mixed together, and the measurement repeated. In order to compare my numbers with those of Glan, I have calculated from the measurements on the strong solutions the part of the light which would be left after passing through a layer of 1cm. thickness of a solution containing 2 gram equivs. of $CuSO_4$ in 1 litre, and from the dilute solutions, the fraction which would remain after passing through 8 cms. of a solution containing 0·25 equivs. The results of the calculation are contained in the following table :—

TABLE X.

Region in Spectrum (mean λ).	$(1-p)$ Conc. Solution.	$(1-p)$ Dil. Solution.	Difference.
612·6	0·078	0·077	+0·001
586·1	0·302	0·259	+0·043
563·6	0·501	0·509	−0·008
543·3	0·701	0·695	+0·006
526·1	0·822	0·811	+0·011
509·7	0·904	0·892	+0·012
493·5	0·950	0·946	+0·004
481·5	0·975	0·968	+0·007

Glan's numbers are given for comparison in Table XI (p. 118).

With the exception of one number in each set of experiments, the differences are all in the same direction. They are, it is true, about the same magnitude as the experimental error, but the circumstance that the two sets of numbers were obtained by

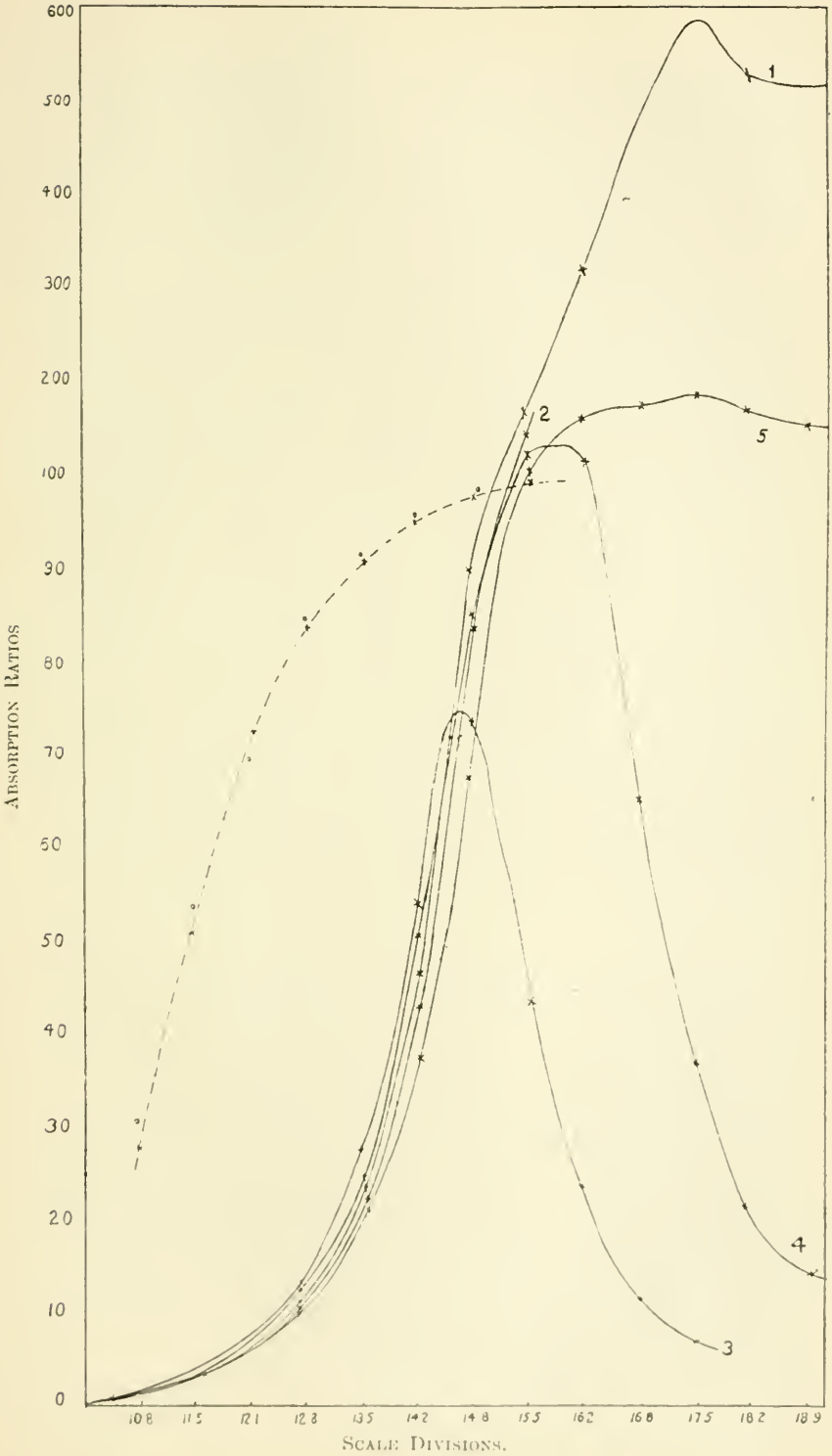
* Glan, *Wied. Ann.* iii. p. 54 (1878)

different methods, and with different instruments, seems to point to the existence of a real difference between the absorption of the strong and dilute solutions of $CuSO_4$. It is not, unfortunately, possible to compare the absolute magnitudes of the absorption, as Glan has only given the relative concentrations of his solutions (last column Table XI). Glan's strongest solutions were, however, evidently saturated, or nearly so, and his experiments are therefore comparable with mine.

Table XI.

Mean λ.	$(1-p)$ conc.	$(1-p)$ dil.	Difference.	Dilution.
674	0·077	0·073	+0·004	1/7
659	0·155	0·150	+0·005	1/7
626	0·336	0·330	+0·006	1/5
557	0·449	0·441	+0·008	1/3
557	0·510	0·507	+0·003	1/7
525	0·822	0·813	+0·009	1/3
525	0·848	0·854	−0·006	1/7

The changes in the absorption spectra of the solutions which occur when the concentration is changed are very clearly visible in the curves which represent the absorption ratios. These are drawn for convenience with the divisions of the tangent screw as abscissæ (instead of wave-lengths), and the values of the absorption ratios as ordinates. Curves 1 and 2 belong to the strong and dilute solutions of copper sulphate; 3 and 4 represent the absorption ratios of the copper chloride solutions containing about 4 and 2 equivalents in 1 litre, and 5 belongs to $Cu(NO_3)_2$. The curves of the most dilute solutions of the three salts lie very close together, and are almost identical with No. 2. The great similarity of the absorptions of these three solutions is best seen, not by comparing their absorption ratios, but by comparing the fractions of the light transmitted by them, calculated for solutions containing the same amount of copper, and for unit length of layer. The comparison is carried out in Table XII. Comparing the absorptions in this way, it is possible to see whether the differences between


600
500
400
300
200
100
90
80
70
60
50
40
30
20
10
0
Absorption Ratios
108
115
121
128
135
142
148
155
162
168
175
182
189
Scale Divisions.
1
2
3
4
5

them are greater than the experimental error or not. This is very difficult when the numbers are calculated as absorption ratios, as the errors in the measurements are much exaggerated in parts of the spectrum where the absorption is small, and *vice versâ*.

TABLE XII.*

Region in Spectrum.	$CuSO_4$.	$CuCl_2$.	$CuSO_4 - CuCl_2$.	$(CuNO_3)_2$.	$CuCl_2 - Cu(NO_3)_2$.
627·7—599·4	0·2775	0·3018	−0·0243	0·3096	−0·0078
599·4—574·2	0·5089	0·5403	−0·0314	0·5430	−0·0027
574·2—551·6	0·7130	0·7157	−0·0027	0·6854	+0·0303
551·6—534·1	0·8333	0·8398	−0·0065	0·8254	+0·0144
534·1—518·2	0·9008	0·9087	−0·0079	0·9069	+0·0018
518·2—502·3	0·9447	0·9474	−0·0027	0·9513	−0·0039
502·3—488·3	0·9725	0·9709	+0·0016	0·9759	−0·0050
488·3—474·6	0·9840	0·9831	+0·0009		

The numbers for copper chloride and copper nitrate are very similar, the differences are scarcely larger than the experimental error and vary in sign. The differences between copper sulphate and copper chloride, on the other hand, are nearly all in the same direction, and sometimes considerably exceed the error of experiment.

CONCLUSIONS.

It is at once noticeable that the curves representing the absorption ratios of all the solutions appear to start out from the same point at the red end of the spectrum, and for a short distance to follow an identical course, diverging more and more widely as the wave-length decreases. It appears natural to attribute this absorption in the red, which is common to all the solutions, to the common constituent copper, and to attribute the differences partly to the absorption exercised by the acid radical itself, and partly to the influence which it has on the vibrations of the copper.

* The numbers are calculated for solutions containing 1 equivalent in 1 litre.

Something analogous to this influence of the acid radical on the absorption of the copper was observed by Abney and Festing* in their work on the absorption spectra of organic and other compounds in the infra-red. They found that a number of definite lines in these spectra undoubtedly were due to hydrogen, but that the number of them and their relative intensity in any spectrum were dependent on the other atoms with which the hydrogen was combined. The investigations of Hartley, Krüss, Vogel, and others on the absorption spectra of organic compounds have shown that the absorption of light by a substance is dependent on its chemical constitution. Every change in the nature, number, or linking of the atoms causes a corresponding change in the absorption spectrum. So that in general when two substances are chemically combined the absorption spectrum of the compound will be different from that of the constituents. On the other hand, when two substances which are not chemically united exist together in a solution, the absorption spectrum is the sum of the two separate spectra. Arguing backwards, it seems probable that, if two substances in a solution absorb light independently of one another, so that replacing one of them by something else makes no difference in the absorption spectrum of the other, then they are not chemically combined. In the dilute solutions of the three copper salts examined this appears to be—at least very nearly—the case. Replacing SO_4 by Cl_2 or by $(NO_3)_2$ makes very little difference in the absorption, though in the strong solutions the difference made by such a replacement is very large. One would, therefore, seem to be forced to the conclusion that only in the strong solutions is the copper really chemically combined with the acid part of the salt, and that as the solutions become more and more dilute the dissociation of the salt becomes greater and greater. It has already been pointed out at the beginning of this paper that in general salts in aqueous solution behave in the same way as these copper salts, though exceptions are known.

It only remains to compare briefly the results thus arrived at with existing theories of solution.

(1) According to the theory of Arrhenius, the electrolytic dissociation in the most dilute copper solutions which were

* *Phil. Trans.* (1881), part III. p. 887.

examined is by no means complete, and therefore the absorption spectra of the three solutions should not be identical.

The degree of dissociation is calculated from the numbers of Kohlrausch* for copper sulphate, of J. Trötsch† and J. H. van 'tHoff and Reicher‡ for copper chloride, and of Long§ for copper nitrate. The numbers obtained are as follows :—

$CuSO_4$, 0·2856 eq. in 1 l., $\mu = 344$, $\mu_\infty = 1086$,
dissociation = 31·7 per cent.
,, 2·38 eq. in 1 l., $\mu = 166$,, = 15·3 ,,
$CuCl_2$, 0·4189 eq. in 1 l., $\mu = 64$, $\mu_\infty = 101$,
dissociation = 63·4 ,,
$Cu(NO_3)_2$, 0·3552 eq. in 1 l., $\mu = 65{\cdot}8$, $\mu_\infty = 100$?,
dissociation = 65·8 ,,

It is interesting to observe that the solutions of chloride and nitrate of copper in which the dissociation is far advanced and nearly to the same extent, possess almost identical absorption spectra, whereas that of copper sulphate is noticeably different, which fact is in agreement with the theory, the dissociation in the copper sulphate solution being very much less advanced than in the others.

It is as well to draw attention to the fact that before one can determine whether the limit of dilution after which the absorption no longer changes is identical with the limit at which the dissociation is complete, it may be necessary to examine the absorption in the ultra-violet and perhaps in the infra-red. The experiments in the first part of this paper with copper chloride seem to show that changes go on in the invisible violet after they have ceased in the visible part of the spectrum.

(2) Knoblauch has explained the alterations in the spectra of certain salts by assuming a hydrolytic dissociation in the more dilute solutions. In the case of the copper salts examined there appears to be no reason for assuming that such a dissociation takes place to any extent. A hydrolytic dissociation of a copper salt would lead (as it does with chromium salts) to a separation of hydroxide. The small amount of precipitate which forms in

* *Wied. Ann.* vi, p. 1 (1879) ; *ibid.* xxvi, p. 188 (1885).
† *Wied. Ann.* xli, p. 259 (1890).
‡ *Zeitschrift. Phys. Chem.* iii, p. 198 (1889).
§ *Wied. Ann.* xi, p. 37 (1880).

solutions of cupric salts after standing for some time appears to be due to impurities in the water (chiefly ammonia and carbon dioxide).

(3) According to the theory of Armstrong* and Traube,† the changes in the absorption spectra which occur on passing from concentrated to dilute solutions are due to the larger aggregates of molecules which exist in the concentrated solutions breaking up into smaller molecules. According to this theory, the molecules of the salt, even in the most dilute solutions, still exist as such; and these dilute solutions might therefore be expected to show characteristic differences, similar to those observed in the strong solutions. This, at any rate in the case of cupric salts, is not the case in the visible part of the spectrum.

(4) The changes of colour which the solutions of copper chloride exhibit when its solution is diluted have long been regarded as due to the formation of different hydrates. If we admit with Pickering the existence of hydrates in dilute solutions containing 1000 or more molecules of water, it is conceivable that two salts of the same metal with colourless acids should have in dilute solution the same spectrum, for the influence exercised on the vibrations of the metal by the acid radical would become negligible compared with that exercised by the 1000 water molecules. Two compounds such as $CuCl_2+1000H_2O$ and $CuSO_4+1000H_2O$ might well have the same spectrum. The experiments are hardly complete enough to allow of any very definite conclusion on this point, but as I am occupied with further experiments on the absorption spectra I hope to return to it on another occasion.

The large changes of colour which often occur on diluting the solutions of the halogen salts of heavy metals may perhaps be connected not with hydrates but with the halogen. Gladstone‡ has pointed out that the spectra of strong solutions of the bromides of platinum, gold, copper, and of potassium palladium bromide, all appear to be made up of the absorptions of bromine water and of a salt of the metal with a colourless acid. It appears as though the halogen when combined with a metal exercised its absorption

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* *J. Chem. Soc.* liii, p. 116 (1888).

† *Berichte* xxiii, p. 3582 (1890).

‡ Gladstone, *Phil. Mag.* [4] xiv, p. 118 (1857).

in the same way as in the free state, but modified to a greater or smaller extent by the metal with which it is combined.

The following is a summary of the results arrived at :—

(1) The absorption spectra of the three salts examined undergo changes on diluting their solutions.

(2) These changes are of such a nature that the spectra tend to become identical in dilute solutions.

(3) The results of other observers show on the whole that salts of other metals behave in a similar way.

(4) The behaviour of the salts examined leads to the conclusion that, in strong solutions, the acid and basic parts of the salts are associated in producing absorption of light, while in dilute solutions they act independently in doing so.

(5) These results are in substantial agreement with the hypothesis of electrolytic dissociation.

(6) The results cannot be satisfactorily explained on the hypothesis of a hydrolytic dissociation, or on that of molecular aggregates.

In conclusion, I take this opportunity of expressing my thanks to Professor H. B. Dixon, at whose suggestion this investigation was begun, and also to Professor A. Schuster for the kindness with which he placed the Vierordt spectro-photometer and other apparatus at my disposal, and for much valuable advice in carrying out the work.

ON NEW FORMS OF STEREOMETERS.

By W. W. Haldane Gee, B.Sc., *and* Arthur Harden, M.Sc., Ph.D.

THE problem of experimentally determining the volume of a body to which the usual hydrostatic methods are inapplicable was first attacked in 1797 by Capt. H. Say (*Annales de*

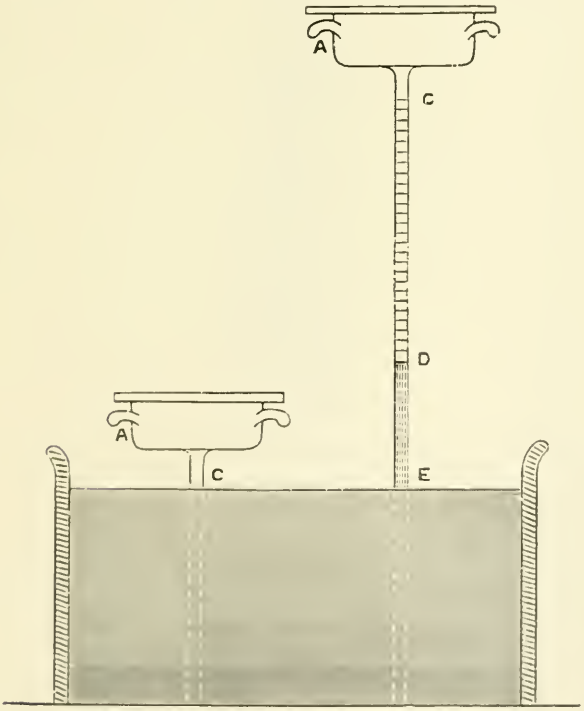


Fig. 1.

Chimie xxiii, 1), who described an instrument (Fig. 1) devised for the purpose of determining the specific gravity of gunpowder.

The vessel A, the stem of which is graduated and calibrated, so that both the distance and also the internal volume of the tube is known between any two graduations, is immersed in mercury up to a fixed mark (C) on the stem. A ground-glass plate is then applied so as to close the vessel airtight. The apparatus is now raised to a convenient extent, and the level of the mercury inside at D and outside at E of the stem noted.

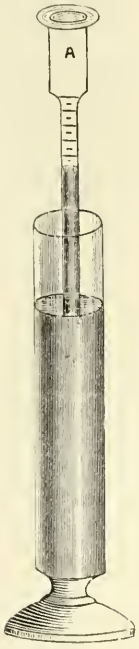


FIG. 2.

The body of unknown volume is then placed in A and the experiment repeated.

I. To find the volume V of the air in the vessel A.

Let the atmospheric pressure... ... ... $= m$

The pressure after lifting, *i.e.*, $m - DE$ ... ... $= n$

The increase of volume CD due to diminution of pressure ... ... $= v$

Then $$V + v = \frac{Vm}{n}$$

and $$V = \frac{nv}{m - n}$$

II. Let x = the volume of the substance,

Then in the second experiment $V - x$ must be written for V, its value calculated and the value of x found by subtraction.

A very similar apparatus (Fig. 2) was described by Leslie in 1826 (*Quarterly Journal of Science and Arts* xxi, 374), and was used by him to ascertain the specific gravity of various powders, such as charcoal, flour, volcanic ashes, &c.

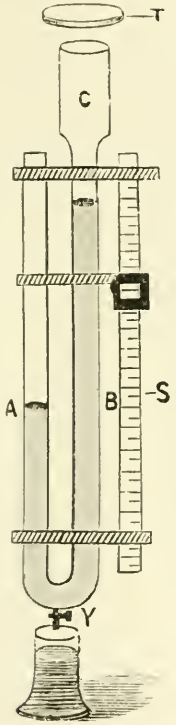


FIG. 3.

To obviate the error arising from absorption of air, he determined the volume with different degrees of dilatation.

W. H. Miller (*Phil. Mag.* [1834], v, 203), in 1834, introduced a considerable improvement in the construction of Say's instrument, which will readily be understood from the accompanying diagram (Fig. 3). Greater accuracy in reading off the height of the mercury, and freedom from the error due to capillary depression, are attained by the use of two parallel tubes. The apparatus was

specially designed for determining the volume of a standard weight, which could not be treated in the usual way. (Cf. *Phil. Trans.*, 1856, 800.)

In 1840, H. Kopp (*Ann. Chem. Pharm.* xxxv, 17) constructed a volumenometer (Fig. 4) in which the pressure of the air is

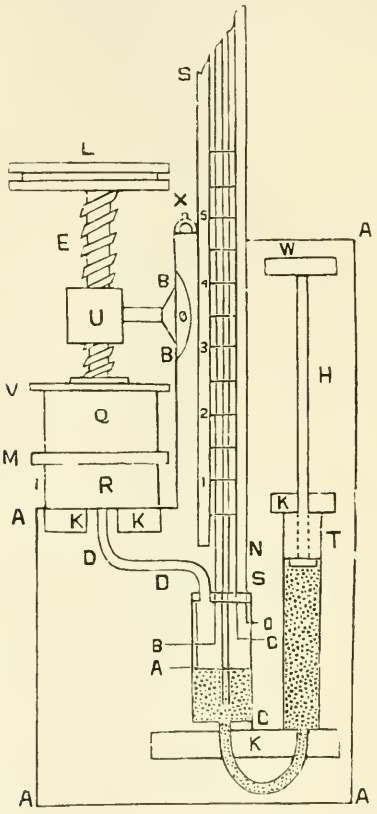


FIG. 4.

increased, instead of being decreased, as in the previous instruments. The ground-glass plate (M) closing the vessel (R) is held in position by a screw L and cork Q, and the volume of air is then diminished by moving the piston in the cylindrical tube (T) until the mercury in C has reached a fixed position marked by needle points in the vessel C (*a*, *b*, *c*, *d*). The pressure required to effect this diminution is read off on the gauge S S. The constants of

the instrument were determined by placing distilled water in R, and no allowance was made for the deviation from Boyle's law shown by air saturated with moisture. The results thus obtained with substances such as tin and lead were exceedingly accurate. It was observed that substances which absorb air, such as charcoal, cannot be employed with this instrument.

Another form of stereometer (Fig. 5) somewhat resembling

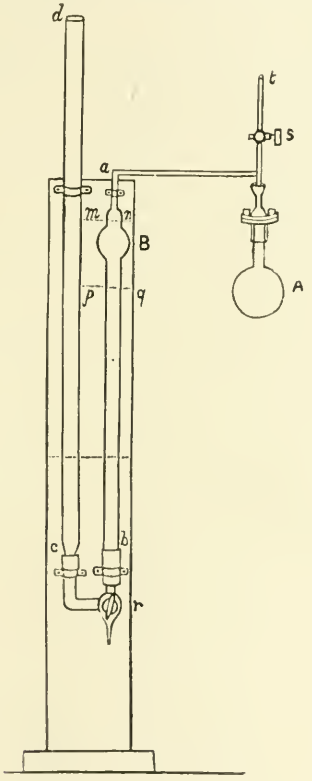


FIG. 5.

that of Miller, was described in 1845 by Regnault (*Annales de Chimie et de Physique* [3] xiv, 207).

In this instrument either decrease or increase of pressure can be employed, and the apparatus is so arranged that it can be filled with dry air. Notice is also made here of the fact that some porous substances absorb air. This is detected by the fact that they give different results according as the pressure is increased or diminished.

A number of determinations has been made by means of this instrument, or an allied form by Grassi, *Annales de Pharmacie et de Chimie* (3) xi, 184.

Buignet, *Ibid* (3) xl, 164.

Fillol, *Annales de Chimie et de Physique* (3) xxi, 417.

Other forms of the stereometer have been designed by :—

Baumhauer, *Archives Néerland* iii, 385 (1868).

Rüdorf, *Wiedemann's Annalen* vi, 288 (1879).

Tschaplowitz, *Zeit. für Analytische Chemie* xviii, 440 (1879).

Paalzow, *Wiedemann's Annalen* xiii, 332 (1881).

Raikow, *Chem. Zeit.* (1888), 525.

A curious instrument of this character was also invented by Harting (*Archives Néerland* vii [1872], p. 289), to determine the volume of the air chambers of living fish.

Notwithstanding the numerous forms of volumenometer which have been described, it is curious that none of them has come into general use for density determinations.

With the object of designing a simple and fairly accurate form of volumenometer, we commenced a series of experiments in the physical laboratory of the Owens College in 1883. It was first of all found that there were so many practical difficulties to be overcome in constructing Kopp's volumenometer, that any idea of employing it as a laboratory instrument had to be given up. The chief difficulty was the construction of a glass cylinder and piston tight to mercury under the pressure of one or two atmospheres. This form of the apparatus was therefore abandoned, and an instrument (which is figured in Stewart and Gee's *Practical Physics*, vol. i) constructed on the type of Miller's stereometer. The pressure was altered, as in the instruments of Regnault and Miller, by running mercury in and out of the apparatus. This process is very objectionable in an apparatus intended for general use, and, moreover, is liable to error on account of the difficulty of getting rid of air bubbles in the narrow parallel tubes.

At this point our experiments were interrupted, and were not resumed until the long vacation of 1889. An instrument was then arranged as shown in Fig. 6.

A glass tube, about 15 mms. in diameter, was constricted at four points, at each of which a cross was etched with hydrofluoric

acid. This tube (A) was firmly clamped on to a vertical wooden stand, and was connected by thick india-rubber tubing (B) with a piece of straight tubing (C) which could be moved up and down in a groove, a millimeter scale being placed between the two tubes. (Another instrument, in which the stereometer tube consisted of a wide tube sealed on to a graduated and calibrated stem,

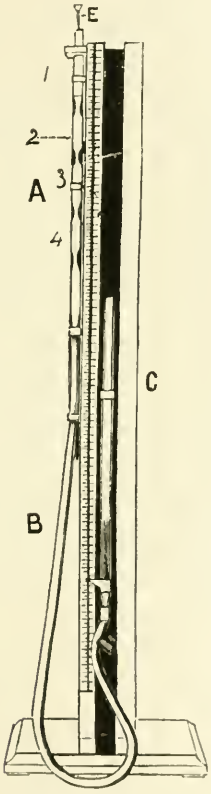


FIG. 6.

was first employed, but did not give quite such good results.) The top of tube A was ground, and could be closed by a small plate of ground glass, which was covered with a thin layer of a mixture of vaseline and bees' wax. By unscrewing the clamps, and adjusting the tube A at the bottom of the stand, the instrument also could be employed with increase of pressure.

The volumes of the several portions of the tube (1, 2, 3, 4) were accurately determined by calibration with mercury. They were as follow :—

1st Instrument : (1) 16·39 c.c.
(2) 10·97 reading on the graduated stem.

2nd Instrument : (1) 15·10 c.c.
(2) 11·06 ,,
(3) 12·15 ,,
(4) 10·00 ,,

In order to test the accuracy of these instruments, the volume of a brass cylinder was determined by their aid, and compared with that found by weighing in water.

To carry out a dilatation experiment the cylinder is placed at the uppermost portion of the tube, the sliding tube adjusted so that the mercury stands exactly at the intersection of the two arms of the etched cross, and the well-greased glass plate then applied, care being taken that the level of the mercury is not altered by this operation. The height of the mercury in the movable tube is then read off on the scale.

The movable tube is then lowered, and adjusted so that the mercury in the other branch is exactly at the level of the second constriction, and the height of the mercury read off as before (in the movable tube). The distance between the two constrictions can be read off once for all, and is, of course, constant. Finally, the height of the barometer is taken.

If V_1 be the volume of the air in the top compartment of the tube, and

V_2 be the volume of the tube down to the second constriction,

P_1 the height of the barometer in mms.,

P_2 the pressure of the air after dilatation, and

x the volume of the cylinder introduced,

then
$$(V_1-x)P_1=(V_2-x)P_2$$

$$x=\frac{V_1P_1-V_2P_2}{P_1-P_2}=V_2-\frac{P_1(V_2-V_1)}{P_1-P_2}$$

The volume of the cylinder employed was ascertained by the hydrostatic method to be 11·828 c.c.

Experiments with 1st Instrument.

	V_1	V_2	P_1	P_1-P_2	x
(1)	16·39	27·66	762·9	541·2	11·78
(2)	16·39	33·01	762·9	59·3	11·79
(3)	16·39	37·86	762·9	626·9	11·73
				Mean	11·77

The error here is ·06 c.c., or ·5 per cent.

Dilatation experiments with 2nd Instrument.

	V_1	V_2	P_1	P_1-P_2	x
(1)	15·10	26·16	764	588·2	11·80
(2)	15·10	26·16	764	588·9	11·82
(3)	15·10	26·16	764	588·3	11·80
(4)	15·10	26·16	764	588·6	11·81
				Mean	11·81

The error here is only ·02 c.c., or ·17 per cent.

The pressure experiments were carried out in a similar manner, the glass plate being secured in its position by the screw E (Fig. 6). In this case, of course, the mercury was set at the lowest constriction, and then forced up to the next, and so on.

P_2 being greater than P_1, and V_1 than V_2, the equation becomes :—

$$x = V_2 - \frac{P_1(V_1-V_2)}{P_2-P_1}$$

	V_1	V_2	P_2-P_1	P_1	x
(1)	48·31	38·31	287·7	764	11·75
(2)	48·31	38·31	287·6	764	11·74
(3)	38·31	26·16	644·0	764	11·75
(4)	38·31	26·16	644·4	764	11·76
				Mean	11·75

The error in this case is ·08 c.c., or ·7 per cent.

This form of the apparatus is therefore fairly satisfactory.

The adjustment of the mercury in the constricted portion of the tube can easily be effected, and the capillary error is removed

by making all the readings on the wide tube (the diameters of the various constricted portions being approximately equal).

It was found impossible to diminish the pressure to less than about 100 mms., as air then passed rapidly through the walls of the india-rubber tubing, although the latter was specially thick, and had been soaked in paraffin (Cf. Roscoe and Lunt, *Journ. Chem. Soc.* [1889], p. 564).

A few experiments were made to determine the sp. gr. of water by this method; 7·1225 grms. of water at 17° were introduced into the apparatus in a small glass tube of volume = 4·097 grms.

In calculating the results of these experiments it is necessary to allow for the aqueous tension (Cf. Grassi., *loc. cit.*).

As before, let V_1, V_2, P_1, P_2 be the actual vols. and pressures.

Then
$$x = V_2 - \frac{(V_2 V_1)}{P_2 - P_1} P_1$$

For P_1 substitute P^1 = Barometer − Aqueous tension.

Then $P_2 - P^1$ = Bar. − Aq. ten. − diff. of level − (Bar. − Aq. ten.), and the equation becomes

$$x = V_2 - \frac{(V_2 - V_1)P^1}{P_2 - P^1}.$$

The water was freed from air by the air pump.

T = 17° B = 763.

	x Observed.	*x* Calculated.
(1)	7·18	
(2)	7·21	
(3)	7·11	
Mean	7·17	7·132

Error = ·038 = ·53 %.

In Grassi's experiments with Regnault's apparatus the error was ·44 %.

Another principle of obtaining the volume of a substance, which, so far as we are aware, has never before been applied, is embodied in the apparatus of Fig. 7.

The glass vessel A and its tubes up to B and B_1 (Fig. 7) are calibrated. The substance of unknown volume is then placed in A, the air of the vessel displaced by pure dry carbon dioxide, which is led in at the three-way tap B and out at B_1, and the weight

of carbon dioxide in the apparatus determined by sweeping the gas out by a current of dry air passed in at D, and absorbing it in a weighed solution of caustic potash. The vessel A is immersed in water, which keeps its temperature constant, and the latter and the height of the barometer are both noted. From these data the volume of carbon dioxide present is calculated, and hence, by subtraction from the known volume of the vessel, the volume of the substance introduced.

The experiments hitherto made show that the volume of carbon dioxide can be easily estimated to within ·3 per cent. of its calculated value, no allowance being made for the small proportion of

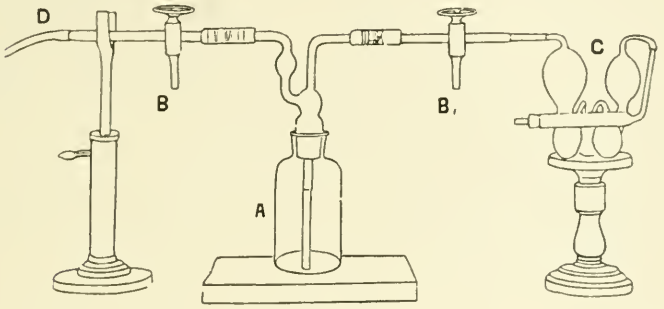


FIG. 7.

air always present (the gas was generated by the action of diluted hydrochloric acid on marble and dried by sulphuric acid). The following results were obtained by gauging the volume of a vessel by this method, the volume being altered by the introduction of brass cylinders of known volume :—

Calculated Vol.	Found.	% Error.
279·13	278·7	−·15
230·47	231·2	+·32
277·79	279·1	+·47
301·45	301·9	+·15
313·27	313·0	−·09

The method is only adapted to the determination of specific gravities when the volume of the substance bears a large proportion to the whole capacity of the apparatus, as otherwise the experimental error is enormously multiplied.

Taking the last number of the above series for example, we have :—

Vol. of apparatus, 325·1 ; Cylinder introduced, 11·83.

		Vol. of Cylinder.	
Vol. of CO_2 (calctd.)	Found.	Calctd.	Found.
313·27	313·0	11·83	12·1
Error % = ·09		Error % = 2·28	

Neither this method, nor the ordinary stereometric one, can be used for a substance such as glass wool. A long series of experiments made by us with this substance shows that its power of condensing gases on its surface is an insuperable obstacle in the way of the determination of its specific gravity by these methods.

The conclusions to be drawn from our experience of these instruments are :—

(1) Their accuracy is inferior to that of the hydrostatic method, which should therefore always be employed when possible.

(2) Porous substances cannot be employed.

(3) The methods of pressure and dilatation should always be both applied.

(4) The air in the stereometer should either be dry or saturated with moisture.

A METHOD OF MEASURING THE VAPOUR PRESSURES OF SOLUTIONS.

By Thomas Ewan, B.Sc., Ph.D. (1851 *Exhibition Scholar in Chemistry at the Owens College*), *and* W. R. Ormandy (*Bishop Berkeley Fellow in Chemistry at the Owens College*).

(From the Journal of the Chemical Society.)

In a note in the *Compt. Rend.* for 1890, cxi, 102, M. G. Charpy has pointed out that a condensation hygrometer, such as Regnault's, may be advantageously used for determining the vapour pressures of aqueous solutions at ordinary temperatures. The same suggestion is made by Ostwald (*Lehrbuch der Allgemeinen Chemie*, 2te Aufl., Band I, 715).* Having occasion to make some determinations of molecular weights in aqueous solutions at the ordinary temperature, we decided to employ this method, and as it appears to be of some practical utility, we publish our results so far as they have gone.

The apparatus which we used is represented in Fig. 1.

The glass vessel A B, which contains the solution under examination, consists of a cylindrical bulb 13 cms. long and 4·5 cms. in diameter, with a narrower neck, 20 cms. long and 2 cms. in diameter. A narrow side tube is sealed (at K) into the shoulder of the bulb, through which the stirrer C passes. This consists of a ring of stout platinum wire, sealed to a light glass handle. The platinum ring just touches the sides of the vessel B, so that they can be kept moistened with the solution.

* Since writing this our attention has been drawn to the work of H. Lescœur (*Ann. Chim. Phys.* [6] xvi, 391, 1889). He has used the method for the determination of the pressure of dissociation of hydrated salts

The hygrometer E F consists of a thin polished silver cup F, soldered to a stronger ring of brass, which in its turn is joined to a glass tube E D. This joint was made by slipping the glass tube inside the brass one, packing the space between them with thin tin foil, and then pouring in melted sulphur. The joint was quite impervious to ether, and by occasionally heating it to the melting point of the sulphur it may be kept quite tight. The upper end of the hygrometer tube at E is closed with a cork, through which

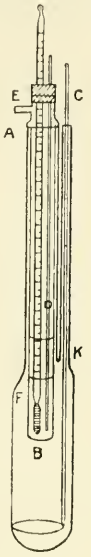


Fig. 1.

pass a thermometer and an open tube, carried down below the surface of the ether in the usual way. A side tube at E is connected with an aspirator in such a way that the amount of air passing through the ether is under the control of the observer. The hygrometer slips loosely through the tube A K, and is supported by an enlargement at A. The whole apparatus was immersed in a water bath holding about 16 litres, and provided with glass windows back and front. The arrangements for keeping it at a constant temperature were very similar to those described by Ostwald (*Zeit. physikal. Chem.* ii, 565, 1888). The stirrer was kept in motion by means of a small water motor. The temperature of the bath seldom varied as much as 0°·1 C. in a day.

The temperatures of the bath and of the ether in the hygro-

meter were read on two thermometers by Hicks, graduated in $\frac{1}{10}$ degrees. As each division was about $1\frac{1}{2}$ mm. wide, $\frac{1}{100}$ degree could be estimated with certainty.

One of the thermometers (69) was correct at zero; its readings were accepted as correct, and the readings of the other thermometer (70) corrected so as to agree with it. The corrections used were at 21°, −0·076; 18°, −0·024; 15°, +0·010.

These numbers are the means of a number of comparisons; a curve was drawn from them, and the corrections to be applied at other temperatures obtained from it.

The experiments were carried out as follows: The vessel B was cleaned by filling it with a mixture of sulphuric acid and potassium dichromate, and allowing it to stand over night; it was then washed with water and dried, and 30 to 40 grams of carefully distilled water were weighed into it, from a pipette of the form used by Beckmann (*Zeit. physikal. Chem.* iv, 548, 1889). The salt was also weighed into B from a tube bent at right angles, so that none of the salt adhered to the neck, A K. This precaution is of some importance, as the hygrometer has to be frequently slipped in and out of the vessel. The solution being made up, the whole apparatus is placed in position in the water bath, and allowed to stand for about 15 minutes, till the air inside becomes saturated with vapour. With dilute solutions this time is ample, but with concentrated solutions we have sometimes observed a small rise in the dew point on standing somewhat longer, owing, doubtless, to the air not being at first fully saturated.

The readings of the dew point were made by simply observing the temperature at which dew first became visible on the hygrometer. We found by a number of preliminary observations that the readings can be made more accurately in this way (when certain precautions are taken) than by the ordinary method. The silver cup of the hygrometer was illuminated by means of a lamp and lens, placed two or three feet behind the observer. The silver surface is looked at through a biconvex lens of small focal length, the eye being in such a position that the light from the lamp is not reflected directly into it.

The dew point being approximately known, the temperature of the ether is lowered rapidly, till it is only one or two tenths of a degree above the point required, after which it is allowed to sink

very slowly. When the dew point is reached, the surface of the silver becomes covered with fine white lines and scratches. After a little practice, the point at which these first appear can be read with certainty. The surface of the silver must be kept very clean. Spots of grease, dirt, &c., which are invisible in the air, become visible as whitish patches on the silver before the dew point is reached, and may lead to too high a reading. We found that the tube could be kept sufficiently clean by means of clean, dry wash-leather and fine jewellers' rouge.

The numbers given in the tables for each solution are the means of three or four readings of the dew point. The greatest difference between two readings was never more than 0·1°; as a rule it was 0·02° or 0·03°.

In order to test the accuracy of our method of reading the dew point, we made a number of determinations of the dew point with pure water. It should of course be exactly the temperature of the bath. The following are the numbers obtained :—

Temp. of bath.	Dew point.	Diff.
18·30	18·30	0·00
18·30	18·29	−0·01
18·29	18·27	−0·02
18·30	18·30	0·00
18·39	18·39	0·00
18·40	18·42	+0·02
18·41	18·42	+0·01

The following tables contain the results obtained with sodium chloride solutions. The letters used have the following significations :—

c = gram molecules of NaCl in 1000 grams of water.

t = temperature of the solution.

t' = dew point.

f' = vapour pressure of water at the temperature t'. (It is also the vapour pressure of the solution at t.)

f/f' is the ratio of the vapour pressure of water to that of the solution, both at $t°$.

The values of f and f' corresponding to the temperatures $t°$ and $t'°$, are taken from the table of vapour pressures for each tenth of a degree calculated by Regnault (*Mém. de l'Acad.* xxi, 627, 1847) from his formula D.

TABLE I.—*Sodium Chloride.*

c.	*t.*	*t'.*	*f'.*	*f*/*f'*.
0·485	20·990	20·718	18·179	1·017
1·047	21·000	20·353	17·775	1·041
1·536	21·018	20·159	17·564	1·054
2·660	21·046	19·504	16·865	1·100
3·044	21·002	19·137	16·487	1·122
4·407	21·000	17·937	15·299	1·209
5·162	21·000	17·281	14·679	1·260
5·307	20·975	16·751	14·197	1·301
0·583	18·103	17·796	15·163	1·019
1·367	18·090	17·382	14·772	1·045
1·564	18·122	17·237	14·639	1·057
2·567	18·025	16·786	14·228	1·081
4·091	18·190	15·480	13·095	1·187
5·292	18·238	14·528	12·320	1·265
0·284	14·825	14·691	12·451	1·009
1·524	14·985	14·147	12·023	1·055
4·852	14·977	11·731	10·276	1·234

As solutions of NaCl follow von Babo's law with close approximation, we have assumed the values of *f*/*f'* observed at temperatures differing slightly from 21°, 18°, and 15° to be the true values at these temperatures. We then take concentrations as abscissæ, and values of *f*/*f'* as ordinates, and draw curves, from which the following table is constructed :—

TABLE II.

c.	*f*/*f'*.			*f*/*f'* (mean).
	21°.	18°.	15°.	
0·5	1·017	1·017	1·017	1·017
1·0	1·038	1·033	1·036	1·036
2·0	1·073	1·067	1·075	1·072
3·0	1·119	1·110	1·122	1·117
4·0	1·183	1·180	1·179	1·181
5·0	1·250	1·247	1·215	1·247
6·0	1·310	1·310	—	1·310

In Table III these results are compared with those obtained by other observers.

Dieterici's numbers (*Ann. Phys. Chem.* xlii, 513, 1891) were obtained at 0° by a method depending on the use of a Bunsen calorimeter. Tammann's numbers were obtained at 100°; they are quoted here from Dieterici's paper. Emden's numbers (*Ann. Phys. Chem.* xxxi, 145, 1887) were the means of values obtained between about 18° and 95°. The numbers in the table we obtained from his results by graphical interpolation.

Table III.

c.	*f*/*f'*.			T. Ewan and Ormandy.
	Dieterici.	Tammann.	Emden.	
0·5	—	—	—	1·017
1·0	1·036	1·033	1·039	1·036
2·0	1·074	1·073	1·080	1·072
3·0	1·120	1·118	1·127	1·117
4·0	1·176	1·171	1·187	1·181
5·0	1·241	1·232	1·252	1·247
6·0	1·315	1·302	—	1·310

We have also made a set of measurements of the vapour pressures of solutions of cupric chloride. The solutions were made up in the way described in the beginning of this paper, from water and crystallised cupric chloride, $CuCl_2,2H_2O$. An analysis of the material used gave the following numbers :—

	Found.	Calculated for $CuCl_2,2H_2O$
Cu.....	37·28	37·32

The salt was prepared by recrystallising copper chloride, bought as pure, from dilute hydrochloric acid, and drying the crystals in an air bath at 45—50°.

The following table contains the numbers obtained. In it

s = concentration of the solutions in grams $CuCl_2$ in 1 gram water.

t = temperature of the solution.

t' = dew point.

f = vapour pressure of pure water at t.

f' = ,, ,, solution ,,

TABLE IV.—*Copper Chloride.*

s.	*t.*	*t'.*	*f.*	*f'.*	*f*/*f'*.	No. of readings of dew point.	Greatest difference between two readings.
0·0169	21·023	20·924	18·521	18·410	1·006	3	0·01°
0·0323	21·010	20·810	18·506	18·282	1·012	2	0·01
0·0560	21·005	20·640	18·501	18·092	1·023	2	0·01
0·0805	20·967	20·322	18·458	17·741	1·040	3	0·02
0·1299	20·920	20·074	18·405	17·472	1·053	3	0·03
0·2018	20·930	19·507	18·417	16·868	1·092	4	0·07
0·2480	20·900	19·001	18·383	16·347	1·125	2	0·02
0·2945	21·040	18·817	18·522	16·162	1·146	3	0·04
0·4398	20·970	17·567	18·462	14·946	1·235	2	0·01
0·0207	18·000	17·855	15·357	15·219	1·009	3	0·01
0·0373	17·950	17·685	15·309	15·058	1·017	2	0·01
0·0736	17·930	17·457	15·290	14·842	1·030	2	0·01
0·1069	17·950	17·218	15·309	14·621	1·047	3	0·01
0·1467	17·983	16·981	15·341	14·404	1·065	3	0·00
0·1798	18·198	16·905	15·550	14·335	1·085	4	0·02
0·3267	18·190	15·712	15·542	13·291	1·169	2	0·00
0·4437	18·190	14·715	15·542	12·470	1·246	4	0·03
0·0207	15·770	15·611	13·341	13·206	1·010	3	0·02
0·0503	15·797	15·463	13·364	13·081	1·022	3	0·03
0·1099	15·920	15·194	13·468	12·859	1·047	5	0·04
0·1631	15·983	14·844	13·522	12·574	1·075	3	0·02
0·2487	16·060	14·266	13·588	12·115	1·122	3	0·02
0·3198	16·032	13·655	13·564	11·647	1·165	4	0·05
0·4099	16·097	13·009	13·620	11·168	1·219	3	0·00
0·5108	16·310	12·117	13·806	10·538	1·310	4	0·14
0·2182	14·425	12·884	12·239	11·078	1·105	4	0·02
0·3147	14·222	11·952	12·080	10·425	1·159	4	0·01
0·3984	14·267	11·223	12·114	9·938	1·219	3	0·02
0·6698	14·808	9·769	12·542	9·028	1·389	5	0·07
0·7489	14·354	8·360	12·184	8·197	1·486	5	0·05

We have attempted using these numbers to calculate the heats of dilution of some solutions of copper chloride by means of the well-known formula of Kirchhoff (*Ann. Phys. Chem.* ciii, 177, 1858, or *Gesammelte Abhandlungen*, 454). This may be written

$$\frac{\delta Q}{\delta m} = -\frac{R\theta^2}{J}\left[\frac{d}{d\theta}\log f - \frac{\delta}{\delta\theta}\log f'\right],$$

where heat given out by the system is considered positive. $\frac{\delta Q}{\delta m}$ may be regarded as the heat evolved on adding 1 gram of water to an infinite quantity of the solution.

R is the gas constant for aqueous vapour. It is assumed here that saturated steam at ordinary temperatures may be regarded as a perfect gas.

θ is the absolute temperature, and J the mechanical equivalent of heat. f and f' are the vapour pressures of water and solution respectively.

$\frac{\delta}{\delta\theta}\log f'$ was calculated from the vapour pressure determinations briefly as follows :—

The values of f', contained in Table IV, were obtained at temperatures differing slightly from 21°, 18°, 16°, and 14°·5 respectively. The numbers corresponding exactly to these temperatures were calculated by assuming that f/f' is constant through the small range of temperature separating the point at which the determination actually took place from that for which the value of f' was required. As this range was generally about 0·1°, the error committed by making this assumption is negligible. From the numbers thus obtained we interpolated the values of f' at the four temperatures above mentioned, for solutions containing 0·05, 0·1, and 0·2 gram $CuCl_2$ in 1 gram of water. For this interpolation we used the following formulæ, in which s is the concentration in grams of $CuCl_2$ in 1 gram water, and $(f-f')$ is the difference between vapour pressure of water and that of the solution :—

$$\left.\begin{aligned}(f-f')_{21^\circ} &= 7{\cdot}6314\,s+1{\cdot}1111\,s^2\\ (f-f')_{18^\circ} &= 6{\cdot}4075\,s+1{\cdot}015\ \ s^2\\ (f-f')_{16^\circ} &= 5{\cdot}3624\,s+1{\cdot}8586\,s^2\\ (f-f')_{14{\cdot}5^\circ} &= 5{\cdot}1525\,s+0{\cdot}6396\,s^2-0{\cdot}46418\,s^3\end{aligned}\right\} \quad . \quad . \quad . \quad (A)$$

We now expressed the numbers thus obtained by means of formulæ of the form given by Magnus, viz. :—

$$f'=a\,.\,10^{\frac{bt}{c+t}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (B)$$

where a, b, and c are constants.

By differentiating the expression B with respect to t, we get :—

$$\frac{\delta}{\delta t}\log f'\left(=\frac{\delta}{\delta\theta}\log f'\right)=\frac{bc\log_e 10}{(c+t)^2}.$$

In order to be able to calculate more accurately the constants of the formula B than was possible by means of the numbers obtained over the small range of temperature through which we were able to use our apparatus, we also made use of the vapour pressures of the solutions at their freezing points. The vapour pressure of an

aqueous solution is at its freezing point the same as that of ice at the same temperature. The freezing points of the solutions were obtained from a set of measurements made by one of us, which are not yet published. The vapour pressures of ice were taken from the table calculated by Ramsay and Young (*Phil. Trans.* pt. ii, 476, 1884); a small correction (0·001—2 mm.) was applied to them, owing to the fact that Ramsay and Young's calculation was based on Regnault's formula E, whilst we used his formula D. The following are the numbers used :—

Table V.

s.	Freezing point.	*f.*	*f'.*
0·05	−1·905	4·010	3·935
0·1	−4·12	3·411	3·258
0·2	−9·63	2·253	1·957

The constants in formula B, which were used, are the following :—

Table VI.

s.	*a.*	*b.*	*c.*
0·05	4·5116	8·4049	271·4
0·1	4·3978	8·1790	262·77
0·2	4·1171	6·9722	217·5

It may be pointed out that the constant a in the preceding table represents the vapour pressure of the solution at 0°.

The tables which follow contain the numerical results of the calculations. In Table VII t = temperature of the solution, f' = its vapour pressure, $(f-f')$ = diminution of the vapour pressure, $(f-f')$ calc. is the diminution calculated by means of the formula A. The difference between the calculated numbers and those found experimentally only in one case exceeds 0·1 mm. The algebraic sum of the differences is approximately zero, so that the formula may be taken as fairly representing the results.

Table VII.

$t = 21°$.

s.	f'.	$(f-f')$.	$(f-f')$ calc.	Diff.
0·0169	18·384	0·111	0·129	+0·018
0·0322	18·271	0·224	0·247	+0·023
0·0560	18·077	0·418	0·431	+0·013
0·0805	17·776	0·719	0·621	−0·098
0·1299	17·557	0·938	1·010	+0·072
0·2018	16·939	1·556	1·585	+0·029
0·2480	16·446	2·049	1·960	−0·089
0·2945	16·138	2·357	2·344	−0·013
0·4399	14·973	3·522	3·572	+0·050
			Sum.....	+0·205 −0·200

$t = 18°$.

s.	f'.	$(f-f')$.	$(f-f')$ calc.	Diff.
0·0207	15·219	0·138	0·133	−0·005
0·0373	15·109	0·248	0·241	−0·007
0·0736	14·907	0·450	0·477	+0·027
0·1068	14·667	0·690	0·686	−0·004
0·1467	14·419	0·938	0·962	+0·024
0·1798	14·157	1·200	1·185	−0·015
0·3267	13·133	2·224	2·202	−0·022
0·4437	12·322	3·035	3·043	+0·008
			Sum.....	+0·059 −0·053

$t = 16°$.

s.	f'.	$(f-f')$.	$(f-f')$ calc.	Diff.
0·0207	13·399	0·137	0·111	−0·026
0·0503	13·249	0·287	0·274	−0·013
0·1099	12·924	0·612	0·612	0·000
0·1631	12·587	0·949	0·924	−0·025
0·2487	12·068	1·468	1·449	−0·019
0·3198	11·623	1·913	1·905	−0·008
0·4099	11·098	2·438	2·510	+0·072
0·5108	10·332	3·204	3·224	+0·020
			Sum.....	+0·092 −0·091

TABLE VII—(*continued*).

$t = 14°{\cdot}5$.				
s.	f'.	$(f-f')$.	$(f-f')$ calc.	Diff.
0·2182	11·131	1·167	1·150	−0·017
0·3147	10·613	1·685	1·671	−0·014
0·3984	10·089	2·209	2·125	−0·084
0·6695	8·852	3·446	3·597	+0·151
0·7489	8·274	4·024	4·023	−0·001
			Sum.....	+0·151 −0·116

Table VIII contains under f' the vapour pressures (interpolated from the formulæ A) of solutions containing 0·05, 0 1, and 0·2 gram of $CuCl_2$ in 1 gram water, under "f' calc." the values calculated from the formulæ B. The agreements between the two sets of numbers is very close indeed.

TABLE VIII.

$s = 0{\cdot}05$.				$s = 0{\cdot}1$.			
t.	f'.	f' calc.	Diff.	t.	f'.	f' calc.	Diff.
21°	18·111	18·112	+0·001	21°	17·721	17·721	0·000
18	15·033	15·035	+0·002	18	14·706	14·668	−0·038
16	13·263	13·251	−0·012	16	12·981	12·962	−0·019
14°·5	12·039	12·040	+0·001	14°·5	11·776	11·776	0·000
−1°·905	3·935	3·935	0·000	−4°·12	3·258	3·258	0·000

$s = 0{\cdot}2$.			
t.	f'.	f' calc.	Diff.
21°	16·924	16·924	0·000
18	14·035	14·044	+0·009
16	12·389	12·370	−0·019
14°·5	11·243	11·229	−0·014
−9°·63	1·957	1·957	0·000

Table IX contains the values of $\frac{\delta Q}{\delta m}$ calculated from Kirchhoff's formula and those obtained from J. Thomsen's numbers.

In Kirchhoff's formula we have

$J = 42355$ grm. cm.

$R = 4709{\cdot}5 \frac{\text{grm. cm.}}{^{\circ}\text{C.}}$.

$\theta = 291$ (Thomsen's experiments were made about 18° C.).

$\frac{d}{d\theta} \log f$ (at 18°) calculated from Regnault's formula D is 0·062653.

Table IX.

s.	m_s.	$\frac{\delta}{\delta\theta} \log f/f'$.	$\frac{\delta Q}{\delta m}$ (E. and O.).	$\frac{\delta Q}{\delta m}$ (Thomsen).	Diff.
0·05	2508	−0·000065	0·61	0·22	0·39
0·1	1164	−0·000129	1·21	0·78	0·43
0·2	492	−0·000313	2·94	2·48	0·46

The numbers in the column $\frac{\delta Q}{\delta m}$ (Thomsen) have been obtained as follows: Thomsen (*Thermochem. Unters.* iii, 113) gives the numbers contained in Table X under Q as the amounts of heat evolved on adding m grams of water to a solution containing 1 gram. mol. $CuCl_2$ in 180 grams of water. The numbers under Q calc. are obtained from the formula given by Thomsen (*loc. cit.*, p. 24).

$$Q = \frac{m}{m + 369{\cdot}5} \times 4976{\cdot}3 ;$$

differentiating this we get :—

$$\frac{\delta Q}{\delta m} = \frac{1838900}{(m + 369{\cdot}5)^2},$$

from which the values of $\frac{\delta Q}{\delta m}$ (Thomsen) are calculated by means of the numbers under m_s in Table IX.

Table X.

m.	Q.	Q calc.	Diff.
180	1630	1630	±0
360	2458	2456	−2
720	3336	3289	+47
1620	4052	4052	±0
3420	4510	4491	−19

Although Thomsen's experimental values of $\delta Q/\delta m$ in Table IX do not agree very well with those calculated from our observations, it is easy to see that very small errors in the determinations of the vapour pressures are capable of accounting for the differences, by adopting the plan originally used by Kirchhoff (*Pogg. Ann.* civ, 612, 1858) of calculating the vapour pressures from the heats of dilution. He transformed the expression already given into the form—

$$\log f/f' = c + \frac{J}{R \cdot \log_e 10} \cdot \frac{1}{\theta} \cdot \frac{\delta Q}{\delta m} \quad . \quad . \quad . \quad . \quad (C)$$

The logarithm is taken to the base 10. c is a constant, and is calculated by means of any one determination of the vapour pressure of the solution. Using the vapour pressures found at 21° in Table VIII we find the values of c :—

s.	c.
0·05	0·006162
0·1	0·008180
0·2	0·005635

In Table XI the numbers calculated from equation (C) by means of these constants are compared with the experimental numbers from Table VIII.

TABLE XI.

$s=0·05$.				$s=0·1$.			
t.	f' calc.	f' found.	Diff.	t.	f' calc.	f' found.	Diff.
−1·905	3·925	3·935	+0·010	−4·12	3·261	3·258	−0·003
14·5	12·041	12·039	−0·002	14·5	11·777	11·776	−0·001
16·0	13·253	13·263	+0·010	16·0	12·964	12·981	+0·017
18·0	15·037	15·033	−0·004	18·0	14·711	14·706	−0·005

$s=0·2$			
t.	f' calc.	f' found.	Diff.
−9·63	2·044	1·957	−0·087
14·5	11·208	11·243	+0·035
16·0	12·370	12·389	+0·019
18·0	14·042	14·035	−0·007

The agreement is on the whole satisfactory.

THE BEHAVIOUR OF ETHYLENE ON EXPLOSION WITH LESS THAN ITS OWN VOLUME OF OXYGEN.

By B. Lean, B.A., B.Sc. *(Dalton Chemical Scholar of Owens College), and* W. A. Bone, B.Sc. *(Fellow of Victoria University).*

(From the Journal of the Chemical Society.)

Introduction.

THIS research, which was made at the suggestion of Professor H. B. Dixon, arose out of an observation made in the course of experiments to determine the rate of explosion of hydrocarbons when fired with an amount of oxygen insufficient to completely burn them. When ethylene was mixed with approximately its own volume of oxygen, and the mixture fired in a long lead coil, it was found that the volume of the mixture was almost exactly doubled, the pressure in the tube having increased from 756 mms. to 1503 mms. of mercury. This result indicated that, in the main, the carbon of the hydrocarbon had been oxidised to carbonic oxide, whilst the hydrogen had been liberated as such; in fact, the result of the interaction could be represented by the equation

$$C_2H_4+O_2=2CO+2H_2.$$

This result corresponds with that arrived at originally by Dalton (*vide* Historical Résumé).

An analysis of the products showed, however, that in addition to small quantities of carbon dioxide and of some unsaturated hydrocarbon, there was also present a small percentage of some hydrocarbon which could not be absorbed by fuming sulphuric acid. We believed this hydrocarbon to be methane, formed by a

partial breaking down of the ethylene molecule, as represented by one or both of the following equations:—

$$2C_2H_4+O_2=2CH_4+2CO,$$
$$C_2H_4=C+CH_4.$$

Another mixture of 2 vols. of ethylene with 3 vols. of oxygen was made, and, on firing this mixture in the coil, the pressure increased from 763 mms. to 1228 mms. of mercury. On analysing the products, no trace either of saturated or of unsaturated hydrocarbons could be detected. It appeared, therefore, interesting to study further the explosion of ethylene with less than its own volume of oxygen. The present paper contains the results of our investigations.

Historical Résumé.

Dalton appears to have been the first to study the incomplete combustion of ethylene. His work, the results of which are given in Part II of his New System, seems to have been overlooked by many subsequent investigators. He found that, on exploding equal volumes of ethylene and oxygen, a great increase in volume occurs, 200 vols. of the mixture, on explosion, yielding 360 vols. Furthermore, the products, when mixed with excess of oxygen and sparked, exploded, yielding carbon dioxide and water. He therefore concluded that the products of the explosion of 100 vols. of ethylene with 100 vols. of oxygen consisted mainly of carbonic oxide and hydrogen, and he estimated that about 170 vols. of each of these gases were thus formed.

Despite Dalton's work, the view became prevalent that, when hydrocarbons undergo incomplete combustion, the hydrogen is burnt to water before the carbon is oxidised.

In 1861, Kersten (*J. pr. Chem.* lxxxiv, 310), who seems to have been ignorant of Dalton's work, arrived at very much the same conclusions. He exploded ethylene with (1) electrolytic gas, (2) defect of air, and his results led him to conclude that the carbon is oxidised to carbonic oxide before the hydrogen is burnt.

In 1874, E. v. Meyer identified minute quantities of acraldehyde among the products of the explosion of ethylene with less than its own volume of oxygen. He explained its formation by the equation

$$C_2H_4+CO=C_3H_4O.$$

The amount produced was too small to admit of a quantitative determination. He, however, failed to produce acraldehyde by sparking a mixture of ethylene and carbonic oxide.

The question of the incomplete combustion of hydrocarbons is, of course, connected with that of the luminosity of hydrocarbon flames. This subject has of late attracted a good deal of attention, owing principally to the researches of Teclu (*J. pr. Chem.* xliv, 246), and of Smithells and Ingle (Trans., 1892, lxi, 204). They find that in an ethylene-air flame the intereonal gases contain acetylene.

V. B. Lewes (Trans., 1892, lxi, 322) concludes that in the inner zone of a non-luminous coal-gas flame the hydrocarbons are heated up by the combustion of the hydrogen and some of the methane, and are resolved into acetylene, which, at a higher temperature, breaks up into carbon and hydrogen.

A correspondence has recently passed between Sir G. G. Stokes and H. E. Armstrong (Proc., 1892, 22) on the interactions occurring in flames. Stokes considers that at high temperatures oxygen combines with carbon in preference to hydrogen. He thinks it necessary to distinguish between the purely chemical and the thermo-chemical changes which occur in partial combustion. Thus, in the ordinary candle flame, purely chemical changes may occur in the blue region at the base and outer portion, where the oxygen is plentiful, and the heat so liberated becomes the cause of thermo-chemical changes which go on in the inner portion of the flame.

Stokes writes: "I imagine that the hydrocarbon spectrum is due to a gas formed by a pure chemical as distinguished from a thermo-chemical change. But what gas is it? It is commonly supposed to be acetylene. To me it seems more probable that it is marsh gas, formed by a pure chemical, not a thermo-chemical, change. According to my notion, this unknown gas (x, say) is a hydrocarbon, which when burnt without admixture of other hydrocarbons would show but feebly, if at all, the hydrocarbon spectrum. More especially might this be expected to take place if it were burnt at a reduced pressure, or considerably diluted with, say, nitrogen. For, in order that it should show its spectrum, its molecule must be in a state of violent agitation, which it might be expected to be if it had been born as a result of partial

combustion, but would not be merely because it was going to be slain by union with oxygen." In a subsequent letter Stokes writes: "The results of Professor Smithells seem to me to make it probable that x may be carbonic oxide."

H. E. Armstrong considers it "unwise at present to infer that the oxidation of the hydrocarbons, or the separation of carbon and also of hydrogen from them, takes place entirely in any one way."

We may here point out that Dalton, Kersten, and others have only shown that carbonic oxide and hydrogen are *eventually* obtained when ethylene is fired with its own volume of oxygen. Their results do not prove that carbonic oxide and hydrogen are the immediate products of the interaction of ethylene and oxygen.

We began this research at the Owens College, Manchester, in October, 1891. Our plan was to make various mixtures of ethylene with less than its own volume of oxygen, and after exploding them, to carefully analyse the products.

Preparation of the Gases.

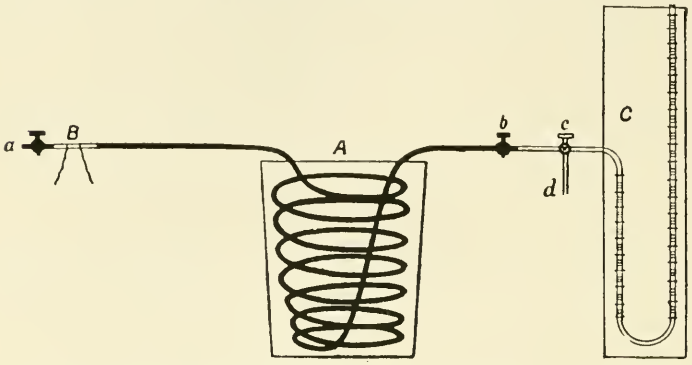
Ethylene.—This was made by Erlenmeyer's method. Into a bolt-head flask was introduced a mixture of 25 grams of alcohol and 150 grams of concentrated sulphuric acid. The mixture was heated up to 160—170°, and this temperature was maintained throughout the preparation. A mixture of 1 part of alcohol and 2 parts of sulphuric acid (by weight) was slowly and continuously dropped into the generating flask from a tap funnel. The ethylene was purified by passing through two wash-bottles containing concentrated sulphuric acid, a tower containing lumps of solid moistened sodic hydrate, then through two wash-bottles containing concentrated soda solution, and lastly a second tower containing solid sodic hydrate.

Oxygen.—By heating potassic chlorate in an iron retort. The gas was purified by passing through a series of wash-bottles and towers containing sodic hydrate, either solid or in solution, and finally, to insure the entire removal of all chlorine, a wash-bottle containing a starch and potassium iodide solution was added to serve as an indicator.

The mixtures were made and stored in a gas-holder over mercury. They were then sampled for analysis in tubes over mercury. The products of explosion were also sampled in similar manner.

Explosion of the Mixtures.

This, on account of the violence of the explosion, was effected in a leaden coil to which a mercury pressure gauge was attached. The following is a diagram of the apparatus. The coil A (capacity



= 2·1 litres) was contained in a bucket of water. The coil had a glass firing piece B, and carried steel taps *a*, *b*. *c* is a glass tail tap connecting the coil with the manometer C.

The gases were introduced into the coil through the steel tap *a*, the products were drawn off for analysis through *d*.

The coil was well dried before use, and tested to prove that all joints were tight.

Seven different mixtures of ethylene and oxygen were made.

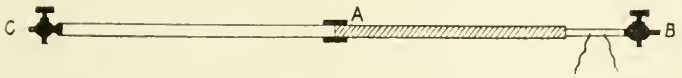
A. We made a mixture of 100 vols. of ethylene with 50 vols. of oxygen. The coil was filled with this mixture, and sparked. The gases only seemed to burn in the neighbourhood of the wires, and on connecting with the manometer no change in pressure was recorded. We then introduced a little electrolytic gas at the firing piece end, in order, if possible, to start an explosion. On sparking, the flame started at the firing piece, but on connecting with the manometer, a slight decrease in pressure was recorded, showing that only the electrolytic gas in the firing piece had been fired. We concluded that a mixture of ethylene with half its volume of oxygen does not explode.

B. We next made a mixture of 100 vols. of ethylene with 65 vols. of oxygen.

Experiment 1.—Introduced the mixture into the coil, and sparked. A flame seemed to start at the firing piece, but on

connecting with the manometer only a very slight increase in pressure (20 mms.) was recorded, showing that the mixture had merely burned in the neighbourhood of the wires. We then sent a little electrolytic gas in at the firing piece end, and sparked. The mixture did not explode.

Experiment 2.—We substituted a wider tube for the coil. A B is a metal tube carrying a glass firing piece, and a steel tap B. This is joined to a wide glass tube, A C, by means of a metal joint at A, and on to this is fixed a steel tap C.



The mixture was introduced into the apparatus, and sparked. The flash, which travelled rapidly along A C, was of intense brightness, and was succeeded by a dense black cloud of liberated carbon. The products were displaced by a current of air, and burnt with a fairly luminous flame at C.

This mixture, therefore, seemed to be near the limit of detonation, it being possible to fire it in the wide tube, but not in the narrower coil.

C. We next made a mixture of 100 vols. of ethylene with 70 vols. of oxygen.

Experiment 1.—Filled the coil with the mixture, and sparked. The mixture burnt in the neighbourhood of the wires only. We then introduced a little electrolytic gas at the firing piece end, and again sparked. The mixture was fired, and the manometer showed an increase in pressure of 480 mms. Carbon was deposited on the glass of the firing piece.

Experiment 2.—We tried to fire the original mixture, after filling the coil at the ordinary temperature, and then heating the water surrounding it up to 85°. On so doing, the gases in the coil were found to be under a pressure of 184 mms. above that of the atmosphere. The mixture was then sparked, but was not fired. On introducing electrolytic gas, however, and sparking, the mixture was fired as in the previous experiment, and the manometer registered an increase in pressure of 466 mms.

D. Made a mixture of 100 vols. of ethylene with 75 vols. of oxygen.

Experiment.—The coil was filled with the mixture, and sparked. No explosion. Introduced a little electrolytic gas at the firing piece end, and sparked. The mixture was fired, and the manometer recorded an increase in pressure of 546 mms. Carbon was deposited in the firing piece.

E. Made a mixture of 100 vols. of ethylene with 90 vols. of oxygen.

Experiment.—The coil was filled with the mixture; on sparking, the flame seemed to start in the firing piece, but did not travel far, as the manometer only recorded an increase in pressure of about 20 mms. On introducing a little electrolytic gas and sparking, the mixture exploded, and the manometer recorded an increase in pressure of 512 mms. of mercury. Much less carbon was deposited than in the previous experiments.

F. Made a mixture of 100 vols. of ethylene with 95 vols. of oxygen.

Experiments.—Filled the coil with the mixture, and sparked. The mixture exploded, and the manometer recorded an increase in pressure of 703 mms. of mercury, the barometer standing at 776·8 mms. On repeating the experiments the increase in pressure recorded was 690 mms. There was scarcely any carbon deposited.

G. This is the mixture which was employed at the outset of the research (see Introduction); it was intended to contain equal volumes of oxygen and ethylene; analysis, however, showed that there was rather less oxygen than ethylene, the real composition being 100 vols. of ethylene to 96·5 vols. of oxygen. The increase in pressure on explosion was 747 mms. of mercury, the barometer standing at 756 mms.

Analysis of the Gases.

Apparatus.—The apparatus employed was a modified form of the McLeod apparatus (described in *Phil. Trans.*, 1884, Part II). This consists essentially of a eudiometer, connected at its base with a barometer; both eudiometer and barometer are water-jacketed, so that the temperature may be kept constant throughout the analysis. Both eudiometer and barometer are connected with a mercury reservoir, which may be raised or lowered as occasion may require. The upper end of the eudiometer is

connected by means of a glass capillary tube with a laboratory vessel, into which the gases are sent for purposes of absorption.

The eudiometer and laboratory vessel are closed by glass taps. Steps were taken to apply a correction for the gas left in the capillary tube between the two taps after each absorption. The taps were lubricated with glacial phosphoric acid.

Before each analysis, the eudiometer was washed out, first with dilute sulphuric acid, and then with water.

Readings were made by artificial light.

Action of Absorbing Liquids on Gases.

The importance of this question became apparent to us while analysing the mixture F, the first we analysed. We found that fuming sulphuric acid undoubtedly absorbs oxygen, as will be shown below.

Action of Fuming Sulphuric Acid on Oxygen.—We analysed the mixture F in two ways: (1) by first absorbing the ethylene with fuming acid, and afterwards the oxygen with alkaline pyrogallol; (2) by first absorbing the oxygen, and then the ethylene. Two determinations were made by each method. The results were:—

	I. Removal of ethylene first.		II. Removal of oxygen first.	
	(1.)	(2.)	(1.)	(2.)
Ethylene.....	51·65	51·75	48·73	48·55
Oxygen	43·21	42·94	45·57	46·22

The question at once arose, whether fuming sulphuric acid has any action on oxygen. This question was decided by further experiment:—

We took a sample of oxygen prepared from potassic chlorate, and, after washing with dilute potash solution to remove traces of chlorine, we treated it in the laboratory vessel with fuming sulphuric acid, and then with dilute potash again. We found that a considerable absorption had occurred; this could not be due to the drying of the gases, as the eudiometer was kept saturated with moisture:—

Oxygen taken after first treatment with dilute potash ..... = 240·5 volumes.
Absorption by fuming acid..... 2·7 ,,

The oxygen was further subjected to the action of fuming acid, and a further absorption of 1·9 volumes occurred. The gas was in contact with the fuming acid about 15 minutes in each case.

We tested the action of fuming acid, in a similar manner, on hydrogen and nitrogen, but found no absorption.*

Action of Alkaline Pyrogallol on Ethylene.—A sample of ethylene was introduced into the laboratory vessel, and allowed to stand over alkaline pyrogallol for a few minutes, in order to remove any traces of oxygen which might be present. The gas was then measured. It was treated in the laboratory vessel with fresh alkaline pyrogallol and re-measured at successive intervals of 20 minutes. On 170 vols. of gas taken we found no absorption.

We also found that alkaline pyrogallol has no action on nitrogen.

Action of Strong Potash Solution on Ethylene.—We examined this at the suggestion of Professor Dixon. We introduced a volume of ethylene into the laboratory vessel, and then treated it with dilute potash, in order to remove any traces of carbon dioxide or sulphur dioxide which might be present; then measured the gas, and subjected it in the laboratory vessel to the action of saturated potash solution. We found that no absorption occurred, although in one experiment we allowed the gas to remain over the concentrated potash solution for 16½ hours.

Analysis of the Original Mixtures.

In each case we adopted one or both of the following methods :—

I. *Absorption Method.*—This consisted in: (1) the removal of oxygen by means of alkaline pyrogallol; (2) the removal of ethylene by fuming sulphuric acid. Nitrogen by difference.

II. *Explosion Method.*—This consisted in adding excess of air free from carbon dioxide and exploding, determining: (1) the contraction on explosion, that is, C; (2) the absorption by potash after explosion, that is, A. In this method it is necessary to add a very large excess of air (nearly 20 times the volume of ethylene present, if the gases are exploded under normal pressure) in order to prevent the formation of nitric acid on explosion. If this be done, C should = A.

* Compare, however, Murray (*J. Chem. Soc.*, 1892, Tr., p. 18). H. B. D.

Mixture C. Explosion Method.—The following are the results of six determinations for ethylene by this method :—

	(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	Mean.
Ethylene..	55·64	56·66	56·12	56·16	56·29	56·30	56·03 p. c.

Nitrogen.—This was determined by exploding the gas with excess of air, removing afterwards both the carbon dioxide and the oxygen at one and the same time by alkaline pyrogallol. The result was N = 4·53 per cent. This agrees well with determinations of nitrogen made by the absorption method, where N = 4·76 ; 4·33 ; 4·43 per cent.

Hence N (mean of the four determinations) = 4·51 per cent.

Oxygen.—By difference = 39·46. This agrees well with the results obtained by both explosion and absorption methods ; the mean of five determinations being 39·22 per cent.

Results.	Ethylene	56·03
	Oxygen	39·46
	Nitrogen	4·51

Mixture D.—In the case of this mixture, air was accidentally introduced into one of the two sample tubes collected ; consequently we were left with only one tube to analyse. We, however, obtained one very good analysis by the explosion method :—

Gas taken.....	73·65		Ethylene..... 54·18
Air added	611·40	This gives	Oxygen ..... 41·52
C	79·70		Nitrogen ..... 4·30
A	79·92		
Nitrogen left...	486·89		

The result for ethylene was confirmed by two other analyses by the explosion method. Here, $C_2H_4 = 54·08$; 54·55. These analyses were, however, not completed, and we decided to take the results of the one complete analysis.

Mixture E.—Five analyses were made, two by the absorption and three by the explosion method ; one of the latter was, however, not completed, and only gave results for ethylene.

Results.

	Absorption method.		Explosion method.			Mean.
	(1.)	(2.)	(1.)	(2.)	(3.)	
Ethylene	49·30	49·17	50·58	49·66	50·12	49 77
Oxygen	45·51	45 14	45·72	46 86	—	45·81
Nitrogen	5·19	5·69	3·70	3·48	—	4·42

Mixture F.—Two analyses by absorption method. Results :—

	(1.)	(2.)	Mean.
Ethylene.....	48·73	48·55	48·64
Oxygen.....	45·57	46·22	45·84
Nitrogen	5·70	5·33	5·52

Mixture G.—One analysis by explosion method. Results :—

Ethylene.....	49·41
Oxygen	47·69
Nitrogen	2·90

Disregarding the nitrogen, we find by calculation :

Mixture C contains 100 vols. C_2H_4 to 70·44 vols. O_2.

,, D ,, 100 ,, ,, 76·63 ,,

,, E ,, 100 ,, ,, 92·04 ,,

,, F ,, 100 ,, ,, 94·26 ,,

,, G ,, 100 ,, ,, 96·52 ,,

Analysis of the Products.

The analysis of the products constituted the most important part of our work.

Method.—The method employed was: (1) removal of carbon dioxide by potash ; (2) removal of unsaturated hydrocarbons, &c., with fuming sulphuric acid ; (3) addition of measured amounts of oxygen and air ; (4) explosion ; (5) determination of the contraction (C) and the absorption (A).

The nitrogen, except in the case of products G, was specially determined by adding excess of air to a measured amount of the gas, and exploding, afterwards removing the carbon dioxide produced and the excess of oxygen by alkaline pyrogallol. The residual nitrogen was then measured. Knowing the amount of nitrogen in the air added, the amount of nitrogen present originally in the mixture could thus be determined.

Calculation from Results.—Below will be given the results of the analyses in percentages, for carbon dioxide, unsaturated hydrocarbons, C and A. The results obtained for C and A cannot, as will be shown below, be explained, if after removal of the carbon dioxide and unsaturated hydrocarbons, only carbonic oxide and hydrogen remain in the mixture. There must be some saturated hydrocarbon present. It is most reasonable to assume

this to be methane. We shall, later on, have something further to say about the composition of the unsaturated hydrocarbons.

Products of G.—The analysis of these products had to be modified somewhat, owing to the fact that the amount of carbon dioxide present was very small, and no unsaturated hydrocarbon was present.

Carbon Dioxide.—The amount present being so small, it was specially determined in large volumes of the gases. Results :—

	(1.)	(2.)	(3.)	(4.)	Mean.
CO_2.....	0·35	0·27	0·33	0·34	0·33 per cent.

Unsaturated Hydrocarbons.—None present. No alteration in volume after treating 367·7 vols. of the product with fuming acid (after removal of the carbon dioxide). This result was confirmed by other determinations.

Residual Gases.—Fresh amounts of the mixed gases were taken and exploded with excess of air free from carbon dioxide, and C and A determined. Excess of oxygen was removed by alkaline pyrogallol, and the residual nitrogen measured.

Results—

	(1.)	(2.)	Mean.
C	99·62	99·88	99·75
A	50·22	50·68	50·45
Nitrogen	0·85	0·70	0·77

We therefore have 0·33 + 0·77 = 1·10 per cent. of carbon dioxide and nitrogen ; hence the residual gases = 98·90 per cent.

From the absorption, 50·45 per cent., must be subtracted 0·33 per cent. due to carbon dioxide present in the gases before explosion ; hence A = 50·12 per cent.

From the above data, if we calculate on the assumption that only carbonic oxide and hydrogen are present, we find—

Carbonic oxide ...	50·12	Total	99·91
Hydrogen	49·79		

This is 1·01 in excess of the total volume (98·90) ; hence there is some other body, presumably methane, present.

Calculating on this last assumption, we have—

Carbonic oxide.....	49·11 per cent.
Hydrogen	48·78 ,,
Methane	1·01 ,,

Products of F.—In all, four analyses were made, two of which

were not completed, but gave results for carbon dioxide and unsaturated hydrocarbons.

Results.

	(1.)	(2.)	(3.)	(4.)	Mean.
Unsaturated hydrocarbons ..	2·31	1·92	2·23	2·10	2·14
Carbon dioxide	—	1·09	0·75	0·99	0·94
C	96·85	95·93	—	—	96·39
A	48·76	49·40	—	—	49·08

Nitrogen. Two Determinations.

	(1.)	(2.)
Volume of gas taken	60·4	56·9
,, air added	319·15	335·7
Residual nitrogen	254·02	266·9
Per cent. nitrogen	2·59	2·39

Mean for nitrogen = 2·49 per cent.

Calculating from the above data, we have—

Unsaturated hydrocarbons.....	2·14
Carbon dioxide.....	0·94
Methane	2·55
Carbonic oxide	46·53
Hydrogen	45·35
Nitrogen	2·49

Products of E.—Two full analyses were made, which afforded very concordant results. In another analysis, the carbon dioxide and unsaturated hydrocarbons alone were determined.

Results.

	(1.)	(2.)	(3.)	Mean.
Unsaturated hydrocarbons ..	2·68	2·82	2·84	2·78
Carbon dioxide	1·28	1·35	1·10	1·24
C	93·84	93·98	—	93·91
A.....	50·30	50·33	—	50·31

Nitrogen.—Four determinations were made, with the following results :—

	(1.)	(2.)	(3.)	(4.)
Volume of gas taken...	47·7	44·2	57·6	81·6
,, air added...	257·35	258·3	293·4	365·55
Residual nitrogen.....	204·75	205·15	233·69	290·96
Per cent. nitrogen ...	2·5	1·90	2·80	2·22

Mean for nitrogen = 2·35 per cent.

Calculating from the above data, we have—

Unsaturated hydrocarbons.....	2·78
Carbon dioxide.....	1·24
Methane	2·52
Carbonic oxide.....	47·79
Hydrogen	43·32
Nitrogen	2·35

Products of D.—Three full analyses were made. In a fourth analysis everything, except A, was determined, whilst in another analysis the amounts of carbon dioxide and unsaturated hydrocarbons alone were determined.

Results.

	(1.)	(2.)	(3.)	(4.)	(5.)	Mean.
Unsaturated hydrocarbons.	4·63	4·30	3·92	2·42	3·58	3·77
Carbon dioxide	2·19	3·18	2 82	2·98	2·84	2·80
C	93·02	91·86	92 51	92 78	—	92 54
A	49·03	48·95	47·82	—	—	48·61

Nitrogen. Two Determinations. Results.

	(1.)	(2.)
Volume of gas taken.....	45·0	48·1
,, air added.....	286·75	281·1
Residual nitrogen	228·28	224·78
Per cent. nitrogen	3·24	2·97

Mean for nitrogen = 3·10 per cent.

Calculating from the foregoing data, we have—

Unsaturated hydrocarbons.....	3·77
Methane	3·77
Carbon dioxide.....	2·80

Carbonic oxide	44·84
Hydrogen	41·72
Nitrogen	3·10

Products of C.—Two full analyses were made.

	Results.		
	(1.)	(2.)	Mean.
Unsaturated hydrocarbons	5·58	5·49	5·53
Carbon dioxide	1·52	1·74	1·63
Nitrogen	5·35	4·97	5·16
C	95·68	95·28	95·48
A	44·33	44·43	44·38

Calculating from these data we have—

Unsaturated hydrocarbons	5·53
Methane	5·96
Carbon dioxide	1·63
Carbonic oxide	38·85
Hydrogen	43·30
Nitrogen	5·16

We may now tabulate the results of our analyses.

Composition of the Mixtures Fired.

Mixture.	C.	D.	E.	F.	G.
Ethylene	56·03	54·18	49·77	48·64	49·41
Oxygen	39·46	41·52	45·81	45·84	47·69
Nitrogen	4·51	4·30	4·42	5·52	2·90

Composition of the Products of Explosion.

Mixture.	C.	D.	E.	F.	G.
Unsaturated hydrocarbons	5·53	3·77	2·78	2·14	—
Methane	5·96	3·77	2·52	2·55	1·01
Carbon dioxide	1·63	2·80	1·24	0·94	0·33
Carbonic oxide	38·85	44·84	47·79	46·53	49·11
Hydrogen	43·30	41·72	43·32	45·35	48·78
Nitrogen	5·16	3·10	2·35	2·49	1·01

Liberation of Carbon.—The blackening of the glass firing piece when the mixtures C, D, and E were fired appeared to prove the liberation of carbon. To confirm this conclusion, a mixture of 100 vols. of ethylene and 90 vols. of oxygen was exploded in the coil, and the products of the explosion were immediately expelled by a current of air, and driven through a tube packed with cotton wool. The wool was rendered completely black by the very finely divided carbon which it abstracted from the gases.

Unsaturated Hydrocarbons.—In the former part of our paper, we stated that Smithells and Ingle, and independently V. B. Lewes, had arrived at the conclusion that acetylene is formed in the inner zone of the non-luminous flame, owing to the breaking up of the hydrocarbons. We therefore were led to see whether we could detect acetylene among the products of the explosion of ethylene with less than its own volume of oxygen.

The ordinary method for the detection of acetylene (by mea s of an ammoniacal solution of cuprous chloride) cannot here be employed, on account of the presence of carbonic oxide among the products. We therefore employed a solution of silver chloride in ammonia. On passing carbonic oxide through this solution for a considerable time, we found that it became brown, and just a trace of a dark precipitate was formed. Acetylene, on the other hand, at once acted on the solution, forming a yellowish-white precipitate of silver acetylide. We found that we could easily, in this way, detect 0·25 per cent. of acetylene in an experimental mixture containing a large volume of carbonic oxide.

Experiment.—We made a mixture of 100 vols. of ethylene and 90 vols. of oxygen, and exploded the same in the coil. After explosion, we passed the products through an ammoniacal solution of silver chloride; silver acetylide was at once formed. We confirmed this by decomposing a portion of this precipitate with concentrated hydrochloric acid, when the characteristic smell of acetylene was obtained. Another portion was dried, and then heated, when it detonated. There could, therefore, be no doubt that acetylene is formed when ethylene is exploded with less than its own volume of oxygen.

In view of the possible connection between the liberation of carbon and the formation of acetylene, it appeared of interest to test the presence of carbon and acetylene in the products of the

explosion of methane with less than its own volume of oxygen. Methane will not detonate unless it is fired with very nearly its own volume of oxygen. Bearing in mind the fact that the carbon of a hydrocarbon appears to be oxidised before the hydrogen, we did not expect to find any carbon liberated when this mixture was fired, and doubted whether any acetylene would be found among the products of the explosion. Such was the case; neither carbon nor acetylene could be detected.

In view of our results, we are inclined to suggest that the acetylene, formed in the combustion of ethylene with less than its own volume of oxygen, originates in the union of nascent hydrogen with nascent carbon at the very high temperature of the explosion. Such a formation of acetylene appears more probable than that it is produced by the direct decomposition of ethylene molecules.

General Conclusions.

1. Our results indicate that when ethylene is fired with its own volume of oxygen, carbonic oxide and hydrogen are eventually obtained, the result of the interaction being represented by the equation

$$C_2H_4+O_2=2CO+2H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

This is in accordance with the previous work of Dalton, Kersten, and E. v. Meyer.

2. When ethylene is fired with less than its own volume of oxygen, we find that methane is formed. The quantity thus produced increases as the quantity of oxygen in the original mixture decreases. This formation of methane has a bearing upon the subject of the interaction occurring in flames, and is interesting in connection with the expression of opinion on the part of Sir G. G. Stokes, cited in the earlier portion of this communication.

We suggest that the heat liberated by the main reaction produces a decomposition of some of the unburnt ethylene into methane and carbon, analogous to the decomposition which ethylene undergoes when passed through a red-hot tube.

The simplest formation is that represented by the equation

$$C_2H_4=CH_4+C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

Methane might also be produced by partial oxidation, according to the equation

$$2C_2H_4+O_2=2CH_4+2CO \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

3. Carbon is liberated.

4. Unsaturated hydrocarbons are formed, of which acetylene forms an important part. We suggest that the formation of acetylene is due to a secondary reaction between the nascent hydrogen formed according to equation (*a*) and the nascent carbon liberated according to equation (*b*), thus:—

$$2C+2H=C_2H_2.$$

In conclusion, we have great pleasure in thanking Professor Dixon for many fruitful suggestions, and for the facilities he has afforded us in the prosecution of our research.

THE ATOMIC WEIGHT OF BORON.

By J. L. Hoskyns Abrahall, B.A. (Oxon.), Ph.D. (Munich), *late Bishop Berkeley Fellow of the Owens College, Manchester.* (*Edited by* T. Ewan *and* P. J. Hartog, *of the Owens College.*)

(From the Journal of the Chemical Society.)

Preface.

THE work recorded in the following memoir was carried out by the author during the years 1889-91 in Professor Dixon's laboratory at the Owens College. It was brought to an end by his untimely death in October, 1891.*

This memoir has been drawn up mainly from the contents of five rough notebooks, which contain the actual record of the author's experiments as they were performed in the laboratory. But certain missing particulars, with regard to the preparation and titrations, the editors have been obliged to fill in from their own knowledge; whilst for others they are indebted to Messrs. Harden, Ormandy, and Stanton, whom they here desire to thank. The atomic weights had in most cases only been calculated approximately from the observations; for the application of corrections, and for the calculations of which the results are now given, the editors are responsible. They feel deeply how much more imperfect must be the present exposition of the research than that which the author would have given; but, as they were better acquainted with its details than any other of his friends, they undertook the task of editing it.

It may be added that a considerable number of bulbs filled with the various fractions of boron bromide, which served for the

* See obituary notice in the *Manchester Guardian*, October 17th, 1891, and in *Chem. Soc. Journ.*, Trans., 1892, p. 486.

last series of determinations, have been preserved. These were intended for additional experiments. The editors hope that, before long, this material may be utilised.—T. E., P. J. H.

Historical Introduction.

The element boron was isolated almost simultaneously by Davy (*Phil. Trans.*, 1808, i, 43) and by Gay-Lussac and Thénard (*Annales de Chimie*, lxviii, 169, and *Recherches Physico-chimiques*, 1811, i, 308), who found, by oxidising boron with nitric acid, that the sesquioxide contains about one-third of its weight of oxygen. This number would give 48 as the atomic weight of boron. Almost at the same time, H. Davy (*Phil. Trans.*, 1809, i, 82) also obtained free boron, and found, by burning it in oxygen, that the oxide was composed of 1 part of boron and 1·8 parts of oxygen, from which number the atomic weight of boron is calculated to be 13·3. The first accurate determination of the atomic weight is due to Berzelius (*Ann. Phys. Chem.*, 1824, ii, 128), who estimated the amount of water of crystallisation in borax. The borax was first fused in order to destroy organic matter, and then recrystallised and dried between sheets of filter paper for twenty-four hours, after which it was powdered and exposed to the air for varying lengths of time in order to get rid of mechanically enclosed water. A weighed quantity of the substance was heated carefully in a platinum crucible until it finally melted at a red heat. Three experiments which gave identical results showed that the percentage of water in borax is 47·1.* The atomic weight recalculated from this number† is B = 11·059.

In 1849 (*Compt. Rend.* xxix, 7 ; and *J. pr. Chem.*, xlvii, 415), Laurent published a further determination of the water of crystallisation of borax. He found that on throwing a piece of iron into melted borax, hydrogen was evolved, and concluded that the whole of the water was not driven off from this salt by simple

* The weights seem only to have been determined to the centigram

† In the following memoir we have used throughout the following atomic weights: O = 16, Na = 23·051, Ag = 107·923, Br = 79·951, the numbers calculated by Clarke (*Constants of Nature*). We have taken H = 1·0077, this number being the mean of the numbers given by Stas (1·0075), Cooke and Richards (1·0083), Noyes (1·0072), Rayleigh (1·0069), and Dittmar and Henderson (1·0085). (*See* Ramsay in the *Year Book of Science* for 1891, p. 132.)—T. E., P. J. H.

fusion. He, therefore, mixed it with about one-tenth of its weight of powdered Iceland spar, and thus obtained the numbers 47·15 and 47·20 for the percentage of water. He did not, however, regard his experiments as very exact. The atomic weights recalculated from these results* are 10·978 and 10·857; mean = 10·917.

Finally, in 1859, Dumas (*Ann. Chim. Phys.* [3] lv, 181) included in his well-known memoir on atomic weights the record of three experiments made by Deville, in which boron chloride and boron bromide were precipitated with silver. The atomic weights recalculated from Deville's experiments* are as follows:—

(*a*) from BCl_3 ..... 10·808

(*b*) from BBr_3..... 10·964

The discrepancies between the results obtained by previous observers led the author to undertake a redetermination of the atomic weight in question. For this purpose, he performed three series of experiments, depending on (1) the estimation of the water of crystallisation in borax, and (2) the estimation of the amount of silver necessary to precipitate the bromine of a given weight of boron bromide (preliminary and final series).

Determination of the Water of Crystallisation in Borax, $Na_2B_4O_7,10H_2O$.

The borax used was recrystallised once slowly, and twice suddenly, from a supersaturated solution in ordinary distilled water, and, finally, a fourth time from a supersaturated solution in redistilled water. The small crystals thus obtained were freed from the mother liquor by means of the water-pump, and allowed to stand in a vacuum of 5 mms. over anhydrous borax for a week.

Owing to the fact that on heating crystallised borax in the air it swells up to an enormous extent, it was found extremely difficult to drive off the water in this way without incurring mechanical loss of the substance. The following process of dehydration was, therefore, used. The borax was weighed in a platinum crucible, and this was supported on a pipeclay triangle, and slipped into a wide glass tube, sealed up at one end. A

* *See* note †, p. 169.

lump of quicklime was then introduced into the tube, and the end closed with a well-fitting india-rubber stopper, through which passed a tube connected with a closed manometer, and, further, with a water-pump capable of reducing the pressure to the vapour tension of water. The end of the glass tube, in which the platinum crucible stood, was placed in an air bath made from a biscuit tin. The crucible was thus heated in various experiments for very different lengths of time (5—20 hours) to between 250° and 300°; but practically the whole of the water that could be expelled at this temperature was found to come off in the first three or four hours. About $\frac{1}{2}$ per cent. of water still remained in the substance after the longest continued heating. To remove this residual quantity of water, the crucible was taken out of the tube and heated over the naked flame of a Bunsen burner until the weight became approximately constant; in some cases the final heating was done with a blowpipe.

The experiments recorded below were only considered by the author as preliminary, and were carried out in order to determine under what conditions they must be performed to be sufficiently accurate for atomic weight determinations.

The following experiment shows that no boracic acid or other substance is volatilised with the water of crystallisation at 265° in a vacuum. A certain quantity of borax was introduced into a tube, a plug of asbestos was then inserted, the tube exhausted, and all the water which came over on heating was condensed and collected. It did not act on turmeric paper, and left no appreciable residue when left to evaporate in the cold over sulphuric acid.

It was, however, found on heating melted borax over a blowpipe that the flame was coloured yellow, which seems to show that it volatilises, at least, to some minute extent, at high temperatures.

It was observed that on prolonged heating over a Bunsen burner, the weight of the crucible and contents, which diminished at first, finally began to increase. This final increase may have been due to absorption of sulphur from the flame.

The following are the results of these preliminary experiments, of which the data are sufficiently complete to allow of an atomic weight being calculated from them.

No. of expt.	Corrected weight of $Na_2B_4O_7+10H_2O$.	Corrected weight of residual $Na_2B_4O_7$.	Percentage of H_2O found.	Atomic weight of B.
A85 ..	7·00667	3·69587	47·2069	10·843
A91 ..	12·95936	6·82560	47·3308	10·593
A113 ..	4·65812	2·45248	47·3504	10·554
A129 ..	7·47208	3·93956	47·2763	10·703
A131 ..	4·94504	2·60759	47·2686	10·719

The numbers of the experiments given in column 1 correspond to the pages of the notebook on which they are recorded. The weights of hydrated and anhydrous borax were corrected for buoyancy in air.

As has already been said, the weight of the fused borax in some cases reached a minimum value, after which it increased. This minimum value (corresponding to the highest percentage of water) has in these cases been taken as the final weight of the fused borax. The weighings (performed by the method of vibrations) were probably accurate to $\frac{1}{10}$ milligram. They have been corrected for errors in the weights used and for buoyancy in air. [For a full account of the application of these corrections see p. 180.] As the fourth place of decimals is probably correct in the actual weighings, the fifth place has been preserved in the corrected numbers.

The following remarks on the single determinations may be of value: In A 91 and A 113 the borax was finally heated in a small Fletcher furnace, capable of melting cast iron easily. In both cases the temperature was, therefore, exceptionally high, and the loss exceptionally great; the atomic weight calculated from the result is therefore low. A 129 and A 131 were the two last experiments made, and are probably more worthy of confidence than the preceding ones. In A 131 the borax was finally fused over the blowpipe. The actual weighings in a given instance are quoted to show the variations which occur on prolonged heating.

Crucible+borax fused with Bunsen burner		27·30345
re-fused	,, ...	27·30462
,,	blowpipe	27·30312
,,	for half an hour	27·30253

The determination of the atomic weight of boron by this method necessitates the determination of the precise range of temperature within which all the water of crystallisation of borax can be driven off, while none of the anhydrous substance is volatilised. That this is no easy matter, the above experiments clearly show. In spite of their apparent concordance,* therefore, Berzelius's results cannot be finally accepted as trustworthy.

[The method is evidently open to objection on another score, viz., that it is exceedingly rare to find bodies which crystallise with an exact number of molecules of water of crystallisation. On the one hand, the mother liquor may be included mechanically; on the other hand, the salt may be slightly deliquescent, or slightly efflorescent. It is quite possible† that the compound $Na_2B_4O_7+10H_2O$ may yield some of its water of crystallisation to anhydrous borax, both bodies tending to form a lower hydrate with a lower tension of dissociation than the decahydrate.—T. E., P. J. H.]

Preparation of Boron Bromide.

a. Preparation of Boron.—The method followed was that described by Wöhler and Deville. A considerable amount of trouble was taken in attempting to purify the borax completely. Pure boracic acid (of commerce) was first boiled with a small quantity of baryta to free it from sulphuric acid, which adheres to it very tenaciously, and was then recrystallised in small portions at one time. The boracic acid so obtained was fused over the blowpipe in a platinum dish, and poured out on to an iron plate, broken up and powdered, and passed through a sieve.

The powdered substance was then heated in an iron crucible with sodium, under a layer of sodium chloride, exactly in the way described by Wöhler and Deville (*Ann. Chim. Phys.* [3] lii, 63, 1858). The mass was poured into hydrochloric acid and filtered, and the boron mud thus obtained was transferred to a platinum dish, and treated with strong hydrochloric acid and ammonium fluoride (to remove iron and silica), the liquid being warmed. It was finally washed with alcohol and hydrochloric

* *See* note *, p. 169.

† This suggestion is due to Dr. Harden.

acid, and alcohol and ether, and dried in a vacuum. It appears that this preparation was not pure, but still contained iron (perhaps in the form of a boride?). A second preparation of boron was made, the fused mass being poured, as before, into hydrochloric acid, and then washed by decantation till free from the acid. As soon as this is the case, the boron begins partly to dissolve, partly to suspend itself in the water, and from these washings, boron free from iron was obtained by precipitating with hydrochloric acid, re-suspending by treatment with potash, and precipitating again with hydrochloric acid. The boron thus freed from iron was then dried on a porous tile in a vacuum for a month. It was found that it was impossible, however, to free it from water in this way, for on heating it in a vacuum at 100°, water, and, at a higher temperature, hydrogen, were given off.

To free the boron from water, and from any oxide which might be formed in the presence of water, a portion of it was washed with alcohol and then with ether; but on heating subsequently to

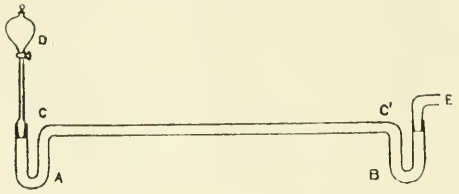


FIG. 1.

this operation, hydrocarbons were evolved, and the attempt to obtain boron free from oxide was therefore abandoned, and it was decided to eliminate the products due to its presence at a later stage.

b. Preparation of the Bromine.—The editors can find no details with regard to the bromine used in Preparation 1 (*infra*). The bromine used in Preparation 2 was made in the following way: A solution of potassium bromide was treated with bromine, and shaken up with pure carbon bisulphide to free it from iodine. The bromide was then crystallised and heated with pure potassium dichromate and dilute sulphuric acid, and the bromine thus obtained was finally distilled over pure, red-hot, electrolytic copper to free it from chlorine. [It is possible that other precautions to ensure its purity were also taken.—T. E., P. J. H.] It was

collected in a stoppered funnel, D, Fig. 1, ground to fit the apparatus for the production of boron bromide.

c. Preparation of Boron Bromide.—Two different preparations of boron bromide were made from the boron obtained in the way described above. In the first only 6 grams of boron were used, and the details given in the author's notebooks are incomplete. This preparation was used for the preliminary set of determinations.

The second preparation was on a large scale, and the editors are able, from their own knowledge, to give somewhat fuller details with regard to it, although no notes on the subject have been preserved.

Preparation 1.—Six grams of boron were first ignited in hydrogen in a hard glass tube placed in an ordinary combustion furnace, to free it from moisture; bromine was then distilled backwards and forwards over the substance heated to redness, the product allowed to stand over mercury till the excess of bromine was absorbed, and then distilled off from the mercuric bromide formed.

Preparation 2.—The apparatus used consisted of a hard glass combustion tube, CC′, Fig. 1, about 1200 mms. in length, to the ends of which were fused the U tubes A and B. The stoppered funnel D, containing the bromine, was ground to fit into the tube A, and the joint well wrapped round with lead foil. The bent neck of the distilling flask E, which contained mercury, was similarly ground into the U tube B.

Bromine was slowly distilled over the red-hot boron placed between C and C′, and the bromide formed, together with the excess of bromine, were finally transferred to the distilling flask. This was then sealed up, and the mixture allowed to remain in it until the colour of the bromine had disappeared. The substance was then redistilled into a clean dry flask of the form shown in Fig. 2, and from this flask it was finally distilled into the tube F, from which it was transferred to the glass bulbs used in the atomic weight determinations*.

* As the boron was not anhydrous, some hydrobromic acid must have been formed during the operation; but it is probable that by the action of the mercury and the mercuric bromide, and the repeated distillation of the boron bromide, it was finally completely eliminated.

The tube A B was about 1 metre long, so that when the flask was exhausted by means of the Sprengel pump, the mercury in the trough C D did not rush back into the flask. A thermometer, E, was sealed into the neck of the flask by wrapping it tightly round with thin lead foil, which, for further security, was enveloped outside with sheet india-rubber coated with coaguline.

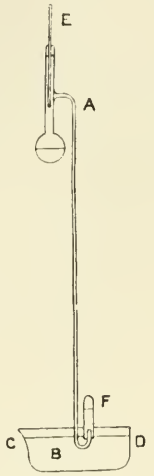


Fig. 2.

The apparatus being so arranged, the boron bromide was distilled in fractions of 10 to 15 c.c. at a time into the test-tube F standing in the trough C D over dry clean mercury.

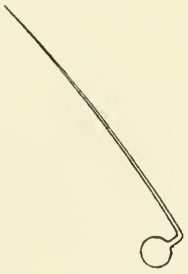


Fig. 3

The separate portions of boron bromide were then introduced into thin glass bulbs of the form shown in Fig. 3, which had been previously weighed. In order to fill each bulb, it was first filled

completely with the mercury. The open end of the capillary neck was then slipped up into the boron bromide at the top of the tube F, and by alternately warming and cooling the bulb with a small flame, the whole of the mercury was replaced by boron bromide. The capillary was then sealed off as close to the bulb as possible, and the neck was preserved along with the bulb to be weighed again.

The bulbs thus prepared always contained a small bubble of gas; this, however, consisted only of the vapour of boron bromide, as on slightly warming the bulb in the hand the bubble could be made to disappear entirely. The size of the bubbles varies rapidly with the temperature, so that boron bromide would appear to have a large co-efficient of expansion.*

---

* *Density of Boron Bromide.*—In order to apply the buoyancy correction to the weights of boron bromide, it was necessary to know the density of the liquid. This was determined (by the editors) with one of the bulbs (6) prepared by the author. The diameter of the bubble of boron bromide vapour resting against the side of the bulb at the temperature of the experiment (16°·5) was found to be 3·3 millimetres; its volume was known to be greater than a hemisphere, and less than a sphere. As the difference between the limiting values is a small quantity compared to the others which entered into the calculation, no sensible error was committed by supposing the mean to be the true value.

The density of the boron bromide was found from the following equation:—

$$d_B = \frac{B}{V - \frac{g}{d_g} - v},$$

where d_B = density of boron bromide.

B = weight of boron bromide (corrected for buoyancy by assuming the density to be that given by previous observers, that is 2·7) = 10·8151 grams. This weight was determined as the difference of the weights of the bulb filled and empty. Strictly speaking, the weight of boron bromide vapour in the bubble should be subtracted from this number, but this weight cannot be more than $\frac{1}{10\,000}$ milligram, and is therefore negligible.

V = the volume of the filled bulb, known by a determination of its loss of weight in water of known temperature = 4·37381 c.c.

g = weight of glass of the bulb = 0·56388 gram.

d_g = density of the glass of the bulb = 2·4679.

v = volume of the bubble = 0·0137 c.c.

Whence we find

$$d_B \text{ (at } 16°\cdot5) = 2\cdot6175.$$

Wöhler and Deville gave the number 2·69, but they do not state the temperature at which the determination was made, and which was probably 0°.

The result given above is of course affected by the uncertainty as to the exact volume of the bubble, but the limiting error in the density cannot amount to $\frac{1}{100}$ of the total value. As the density was only required to correct the weighings, greater accuracy was not attempted. T. E., P.J.H.

Preparation of the Silver.

The silver used was prepared in various ways :—

(*a*) Was obtained as chemically pure from Schuchardt.

(*b*) Was prepared by reducing silver nitrate with ammonium sulphite in the presence of copper, according to the method described by Stas.

(*c*) Was made by reducing silver chloride with milk sugar, but the method used differed somewhat from that of Stas, and is therefore described. About 60 grams of recrystallised silver nitrate were fused till a small quantity of silver had been reduced ; the melt was dissolved in 250 c.c. of water, filtered, and the solution diluted up to 3 or 4 litres. It was then precipitated by means of pure dilute hydrochloric acid, and the silver chloride formed was washed by decantation, and digested with aqua regia in the cold. It was then again washed and dissolved in 1 litre of water, saturated with ammonia, and filtered. 100 grams of twice recrystallised milk sugar were dissolved in 1 litre of water, and filtered into the silver solution. The mixture was allowed to stand for a day in the cold, then warmed, and finally boiled. The reduced silver was washed by decantation, first with cold water, and then with boiling water. The water used had been carefully redistilled from an iron can provided with a block-tin condenser. The silver obtained by the method described is in an extremely finely divided form, and the washing was very tedious. It was collected and melted on lime in the oxy-coal-gas blowpipe, care being taken to use an excess of oxygen. The silver used in the final set of determinations was then purified by electrolysis in the following way. Part of it was dissolved in nitric acid, and the solution of silver nitrate was placed in a platinum dish, which formed the negative pole. The positive pole consisted of the remaining portion of the silver suspended in a linen bag, and connected to the battery by a platinum wire. The bag was hung from the top of a bell-jar, which protected the solution from dust. A tangent galvanometer was included in the circuit, and the current regulated to the strength which was found by Lord Rayleigh and Mrs. Sidgwick (*Phil. Trans.*, 1884, ii, 411) to give the best results with the silver voltameter. Black crystals (of

peroxide?) were formed in very small quantity, which grew in long, hair-like filaments, and sometimes reached from the dish across to the bag. They were, however, isolated, and easily removed (the silver, on melting in a vacuum, gave off no oxygen). The metal obtained was granular and brilliantly white.

The electrolytic silver was placed in a boat cut from a block of quicklime, and melted in a porcelain tube in a vacuum.

Weighings.

The weighings were all performed with a Ladd and Oertling balance provided with an optical arrangement for estimating accurately the amplitude of the swings of the pointer. [The balance has been described by Wills, *Chem. Soc. Trans.* xxxv., 707, 1879.] All weighings were made by Gauss' method. The object to be weighed was first placed on the left-hand pan, four sets of vibrations (each consisting of five or seven swings past the centre of the scale) were taken, and the position of the zero was calculated. This operation was repeated with the object to be weighed in the right-hand pan, and finally again with the object in the left-hand pan. The difference between the two weighings with the object on the left-hand pan never amounted to more than $\frac{1}{20}$ milligram, and generally was less than $\frac{1}{40}$. The mean of the two weighings with the object in the left-hand pan was, of course, in all cases taken. The difference between them was due to a slow change of the zero point which was found to be continuous throughout the series of operations. Such variation did not therefore introduce a sensible error into the weighing.

The temperature of the air in the balance case, and the barometric pressure, were noted for each weighing. The air was assumed to be dry, as fresh calcium chloride was kept in the case.

The errors of the weights were determined three times in the course of the work, before each prolonged set of weighings. As two of the 1-gram weights happened to be precisely equal in weight, they were taken as standards.

The only weights for which the corrections varied more than one or two hundredths of a milligram were the 10-gram weight and the 5-gram weight. The correction for the 10-gram weight

varied 0·6 milligram, and that for the 5-gram weight 0·3 milligram, during the three years over which the work extended.

The weighings of boron bromide (A) and of silver (B) were corrected for buoyancy in air by the following formulæ:—

(A.) Corrected weight of BBr_3 =

$$W - w + \sigma\left[\frac{W-w}{2{\cdot}617} - \frac{W_B - w_B}{8{\cdot}28} - \frac{W_p - w_p}{21{\cdot}23}\right],$$

(B.) Corrected weight of Ag =

$$W + \sigma\left[\frac{W}{10{\cdot}5} - \frac{W_B}{8{\cdot}28} - \frac{W_p}{21{\cdot}23}\right],$$

where W is, in A, the apparent weight in grams of the bulb full of boron bromide in air, and in B the apparent weight of silver in air.

w is the apparent weight of the glass bulb in air.

σ is the weight of 1 c.c. of air at the temperature and pressure noted during the weighing.

W_B and w_B are the brass weights used in making up the weights W and w.

W_p and w_p are the platinum weights used in making up the weights W and w.

[The correction for the rider is negligible.]

2·617 is the density of boron bromide.

8·28 is the density of the brass weights.

21·23 is the density of platinum (Everett).

10·5 is the density of silver.

The density of the brass weights was determined by weighing the 50-gram weight in water. The error introduced by the difference between the actual density of the platinum weights used and the average of the numbers given in Everett's *C.G.S. Units*, which has been taken, could not introduce a sensible error into the experiments.

Titration of Boron Bromide.

When the weight of boron bromide in the bulb chosen for an experiment had been determined, a lump of silver was cut off from the mass, and reduced very nearly to the proper amount by means of a sharp, hard-steel chisel. It was next washed with dilute hydrochloric acid, ammonia, and water, and heated before the final weighing. It was then dissolved in nitric acid in a

stoppered bottle. The bottle had walls about $\frac{1}{4}$ inch thick, and the stopper was ground in with care. When the silver was all dissolved, the bulb of boron bromide was introduced, the stopper inserted, and the bottle shaken so as to break the bulb. The sudden pressure, due to the evolution of gaseous hydrogen bromide, which did not immediately dissolve, was so great as to burst the bottle in some cases, a number of determinations being thus lost. Some bottles specially made for the purpose were used in the final determinations, of which one or two alone proved satisfactory.

The titrations were carried out by a method which in its essentials is that of Stas. A solution of silver nitrate was made up so that 1 gram of solution contained exactly 1·09 milligram of

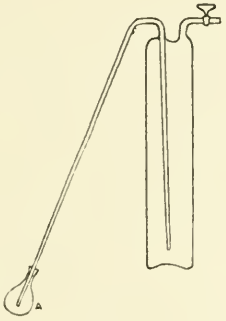


FIG. 4.

silver, and a potassium bromide solution was prepared which was exactly equivalent to it (by weight). These solutions were introduced into pipettes of the form shown in Fig. 4. The small glass cap A was ground on to the end of the siphon tube, so as to prevent loss of liquid when the pipette was not in use. The pipettes were weighed (to the milligram) before and after each addition of solution.

The bottle was placed in a wooden box, blackened internally, and could be illuminated by the rays of a lamp, which were spread out into a flat pencil by means of a glass cylinder, placed with its axis horizontal. The slightest turbidity in the liquid could thus be detected after the addition of silver or bromide solution. Before repeating the addition of either solution, it was found advantageous to filter the supernatant liquid through a small filter into a test-glass, leaving the curdy mass of silver bromide at the bottom of

the bottle. The filtered liquid was then poured back into the bottle, and tested afresh with bromide or silver solution, as the case might be. Towards the end of the reaction, a considerable time was allowed to elapse between the successive additions of these solutions; often only two or three drops were added in a day, so that each titration required a week or more for its completion.

It is well known that some excess of one (say, the silver) solution may be added before an additional drop ceases to produce a visible cloud; and after this point has been reached, a not inconsiderable amount of the other (say, the bromide) solution must be added before an additional drop of this solution ceases to produce a cloud. The silver solution was therefore first added, until the no-turbidity point was attained; the process was repeated with the bromide solution, and again with each solution alternately several times. It was assumed that half of the bromide solution added after silver had ceased to produce a visible reaction was equivalent to the excess of silver present at the beginning of this operation, and that the other half was itself present at the end of the operation as excess. Then, on adding the silver solution again, half the amount added was regarded as equivalent to the excess of bromide in the liquid, while the second half as before remained in excess at the end of the operation. In this way, the excess existing at the previous stage could be calculated from each addition of bromide or silver solution after the first. The mean of all the numbers thus obtained was taken to be the true excess present after the first addition of silver or bromide solution. In this way, the exact weight of silver necessary to precipitate the bromine in a known weight of boron bromide could be determined.

The atomic weight of boron was calculated from the experimental numbers by the formula

$$B = 3AgX - 3Br,$$

where B, Ag, and Br are the atomic weights of boron, silver, and bromine respectively, and X is the ratio of the weight of boron bromide taken to the weight of silver necessary to precipitate the bromine it contains.

Ag was taken = 107·923, Br = 79·951 (*see* note †, p. 169).

The following table gives the experimental data and atomic weights calculated from them :—

TABLE II.*—*Preliminary Series of Determinations.*

Fraction.	No. of bulb.	Weight of boron bromide.	Weight of silver weighed out.	Deficiency or excess determined by titration.	Total silver.	Ratio X = boron bromide / silver.	Atomic weight of boron.
—	10	1·31203	2·84299	+0·00165	1·69406	0·774489	10·902
			−1·15058				
—	7	4·39944	5·67589	+0·00240	5·67829	0·774783	10·998
—	4	5·04022	6·50785	+0·00035	6·50820	0·774441	10·887
—	1	6·51597	8·38890	+0·00029	8·38919	0·774326	10·850
—	9	7·75343	10·01369	−0·00134	10·01235	0·774388	10·870

It must be borne in mind that a given percentage error in the determination of X will produce a relative error 23 times as great in the value of B, a result which may easily be deduced from the equation given above, $B = 323{\cdot}769X - 239{\cdot}853$, if we replace X by its approximate value 0·774. The author was, of course, aware of this, but the method described was chosen, nevertheless, as the most accurate one available.

The close agreement of determinations made with the various fractions of boron bromide of Preparation ii (Table III) affords strong evidence that the substance was in a state of all but absolute purity. It must, however, be noticed that—

(1) The pairs of experiments made with the same fractions, namely 23 and 25, and 32 and 34, yield results which differ only by the $\frac{1}{6000}$ part of their value, and that this may probably be considered as the experimental error to which determinations made with the same fraction were liable.

(2) The two results deduced from experiments made with the first fraction differ in a relatively marked way from the other five results.

* The editors hesitated to insert this table, as the numbers are without comparison less concordant and trustworthy than those of Table III, but have decided to do so for the sake of completeness.

They have purposely omitted to calculate a mean atomic weight from the observations, as the author regarded them as purely preliminary.

TABLE III.—*Final Series of Determinations with Boron Bromide.*

Fraction.	Number of bulb.	Weight of boron bromide.	Weight of silver weighed out.	Deficiency or excess of silver determined by titration.	Total silver.	Ratio X $=\frac{\text{boron bromide}}{\text{silver}}$.	B = atomic weight of boron.
i	23	4·467835	5·769480	+0·001788	5·771268	0·774152	10·794
i	25	8·423151	10·880752	−0·000104	10·880648	0·774143	10·792
ii	19	1·655111	2·136486	+0·001107	2·137593	0·774288	10·838
iii	10	8·032352	10·373182	+0·001019	10·374201	0·774262	10·829
vi	32	4·092743	5·286621	−0·000672	5·285949	0·774268	10·831
vi	34	2·389993	3·086793	+0·000049	3·086842	0·774254	10·826
xi (?).....	11	7·721944	9·974278	−0·000224	9·974054	0·774203	10·811

Mean of all the determinations.. 10·817
Mean error ..... ±0·016
Probable error ..... ±0·0047

Atomic weight determined from the ratio of the total quantity of boron bromide to the total quantity of silver employed in all the determinations = 10·812.

Mean of the last 5 determinations (excluding those made with the first fraction) ..... 10·827
Mean error..... ±0·007
Probable error ..... ±0·003

Atomic weight determined from the ratio of the total quantity of boron bromide to the total quantity of silver employed in the last 5 determinations = 10·823.

(3) Boron chloride has a lower boiling point than boron bromide, and if any of this substance were present as an impurity in the bromide, the major portion of it would distil over with the first fraction, and the atomic weight calculated from the determinations made with this fraction would, therefore, be too low.

Hence it would seem preferable to neglect the first two results, and to consider as the atomic weight yielded by these determinations the number calculated from the last five results.

The number thus obtained, $B = 10{\cdot}825$, is, it will be seen, lower than that given by previous observers, and, moreover, differs considerably from the nearest whole number.

THE ATOMIC WEIGHT OF PALLADIUM.

By G. H. Bailey, D.Sc., Ph.D., *and*
Thornton Lamb (1851 *Exhibition Scholar, Owens College*).

(From the Journal of the Chemical Society.)

THE atomic weight of palladium was first determined by Berzelius (*Ann. Chim. Phys.* viii., 177) in the year 1813 by a synthesis of the sulphide, and by the reduction of the chloride by means of mercury. The values obtained from these experiments were 711 and 704 respectively (oxygen = 100). Fifteen years later (*ibid.* xiii., 454), having recognised that these numbers could not be regarded as very accurate, he repeated the determination, using potassium palladious chloride. He found this difficult to prepare in the anhydrous condition without running the risk of decomposing the salt, but, notwithstanding this, he estimated after reduction in hydrogen—

a. The amount of palladium in a given quantity of the salt.

b. The amount of potassium chloride washed out from the residual palladium.

c. The chlorine given off when the salt is strongly heated.

His numbers, as deduced from these experiments, and recalculated by Clarke (*Constants of Nature* v, 257), are :—

From percentage of metal	.....	106·612
,, KCl	.....	104·674
,, chlorine	.....	110·796

Berzelius himself accepted the first of these values as representing the atomic weight of palladium.

In 1817, Quintus Icilius published a dissertation in which he refers to some experiments done by himself, which led him to take 111·879 as the atomic weight of palladium.

At the time we commenced our investigation, these were the only estimations which had been made, though, while our work was in progress, a paper was published by Keiser (*Amer. Chem. Journ.* xi, 398), from which it appeared that he had used in his determinations palladammonium chloride, $Pd(NH_3Cl)_2$, a salt which our preliminary investigation had already led us to adopt as apparently well adapted for the purpose. It does not, however, appear from Keiser's paper that any special precautions were taken to insure the purity of the palladium used; moreover, the details given with regard to the preparation of the salt and its analysis are too meagre to enable us to draw conclusions as to the cause of the difference between his results and those we have obtained.

The value assigned as the result of these experiments, viz., 106·35, is almost identical with that of Berzelius already quoted.

In view of the importance of a redetermination of the atomic weights of the platinum metals, and of the interest which attaches to the work done during the last few years by Seubert and others, we decided to continue our investigation, especially as, from a communication kindly made to us by Professor Seubert, it appeared that he had no immediate intention of entering upon a redetermination of this atomic weight.

Preparation of Palladium.

The raw material for the preparation was obtained from the Sheffield Smelting Company, and consisted of residues rich in palladium which had been accumulated by them for some time. It was found to contain about 95 per cent. of palladium associated with small quantities of other platinum metals, chiefly platinum, and also copper and iron.

The material was first extracted with hydrochloric acid, and when nothing more passed into solution, the residue was separated by filtration, washed, and dissolved in *aqua regia*. The small quantity of insoluble matter was then removed, and the solution boiled down several times with hydrochloric acid until the nitric acid was entirely expelled. The palladious chloride thus obtained was precipitated by means of mercuric cyanide, the precipitate washed thoroughly (a very slow process, owing to its gelatinous character), and ignited. The metal left on ignition was redissolved in hydro-

chloric acid with the addition of some nitric acid as before, and then thrown down by means of potassium chloride prepared by Stas' method; the potassium palladious chloride thus obtained being reduced in hydrogen and washed till free from potassium chloride. This treatment was repeated several times.

The metal finally obtained was practically unacted upon by hydrochloric acid. It was again dissolved, the excess of acid expelled, and ammonia added until the precipitate at first thrown down was redissolved, a slight residue which remained being rejected. Gaseous hydrogen chloride was then passed into the clear solution after it had been sufficiently diluted to prevent the precipitation of ammonium chloride, and the yellow palladammonium chloride precipitate collected in several fractions. The earlier and later fractions were rejected, the palladium used in the investigation being obtained from the intermediate portions by reduction in hydrogen.

Examination of Salts of Palladium.

The salts investigated were those which seemed likely to be suitable for our purpose, namely:—

a. Palladious cyanide.

b. Palladammonium cyanide.

c. Potassium palladious chloride.

d. Palladammonium chloride.

Palladious Cyanide.—It was found that on heating a small quantity of this salt in the apparatus already described by one of us (*Chem. News* liv, 302), and gradually raising the temperature, no cyanogen was evolved, and the weight remained constant at 220°. An analysis showed, however, that a small quantity of water still remained attached to the salt, and when it was sought to get rid of this by heating to a still higher temperature, decomposition ensued, accompanied by the formation of paracyanogen. The cyanide is, therefore, not adapted for the determination of an atomic weight.

Palladammonium Cyanide.—This was prepared by passing pure hydrogen cyanide into an ammoniacal solution of palladious chloride and recrystallising the salt which separated out. It was obtained in splendid crystals, and appeared to be a most promising substance.

Some difficulty was experienced in obtaining it perfectly anhydrous, but this was overcome. Even below 100° the salt begins to give off ammonia, and it was thought that a determination might be made (*a*) of the ammonia, (*b*) of the palladious cyanide then remaining, (*c*) of the palladium ultimately left by the ignition of the palladious cyanide. It was found, however, that there was no sharp line of demarcation in the decomposition, so that, in view of the advantages presented by the corresponding chlorine derivative, the latter seemed preferable, more especially as at that time we were under the impression that it would be possible to separately determine the chlorine and the palladium, if not also the ammonia in it. Some determinations which were made with this cyanide, however, rendered it probable that the atomic weight did not exceed 106.

Potassium Palladious Chloride.—The difficulty of obtaining this salt in an anhydrous condition, originally pointed out by Berzelius, constitutes a real objection to its use for an atomic weight determination. This objection, however, entirely disappears if, instead of taking the relation between the *salt* and its constituents as he did, we ascertain the ratio which the constituents potassium chloride and palladium bear to each other. This ratio is manifestly independent of the presence of moisture in the salt.

A quantity of the double salt was therefore prepared by precipitating a concentrated solution of palladious chloride by means of potassium chloride, avoiding the presence of oxidising agents. The crystals were carefully separated from the mother liquor, several times washed with small quantities of water, and dried at the ordinary temperature under reduced pressure.

The salt was then heated in a stream of pure, dry hydrogen at as low a temperature as possible until complete reduction had taken place.

TABLE I.

Denomination of sample.	KCl found.	Pd found.	Atomic weight of Pd, H = 1.
K I.....	1·49767	1·05627	104·945
K II	0·90484	0·63738	104·820

In consequence of the difficulty of preparing the pure salt in sufficiently large quantity, and the errors incidental to its analysis,

we at the time saw no hope of achieving results at all comparable in point of accuracy with those attainable from palladammonium chloride. With a larger amount of pure material, such as we at present have, and the experience gained from the determinations made, we believe, however, that a good result may yet be arrived at by this method, and shall take some future opportunity of continuing the investigation along these lines. We have every reason to consider the values deduced from the experiments quoted to be too low.

Palladammonium Chloride.

This salt can be obtained in a very pure condition, as already described in the preparation of palladium, and when the earlier and later portions are rejected several fractions can be obtained which show no appreciable variation in character or composition. It separates out in exceedingly minute, pale yellow crystals, and, after decanting the mother liquor, the product is washed repeatedly by aid of the filter pump. It is practically insoluble in water or dilute acids, and can be readily dried under diminished pressure at the ordinary temperature. It possesses the further advantage of not being hygroscopic, and on several occasions portions of a gram or more having been exposed to air increased in weight two or three tenths of a milligram during the first hour, and after that showed little or no further variation.

Determination of Chlorine.

Method of Analysis.—From 1·5 to 3 grams of the salt were weighed out in a porcelain boat, and reduced by heating in a stream of hydrogen. The hydrogen was prepared from pure zinc and sulphuric acid, and passed successively through alkaline permanganate of potash, nitrate of silver, and potash, and then over a layer of glass wool. The combustion tube used was about 6 feet in length, two-thirds of it projecting outside the furnace, so that the greater part of the ammonium chloride formed in the decomposition might condense in this part. Ammonium chloride was prevented from depositing on the fore part of the tube by heating this first, and also by carefully regulating the supply of hydrogen. Notwithstanding all possible precautions, however, it was not found possible to condense the whole of the ammonium chloride in the tube.

The ammonium chloride washed out of the tube, and that which was carried over into the wash bottles succeeding it, was precipitated by the addition of silver nitrate, using all the precautions adopted by Stas. In some of the experiments the silver chloride was determined gravimetrically. The following table gives the results obtained :—

TABLE II.

Denomination of sample.	$Pd(NH_3Cl)_2$ taken.	AgCl found.	Atomic weight of Pd. O = 1.	Atomic weight of Pd. H = 1.
B II.....	1·24276	1·682249	6·6771	106·566
R II.....	1·08722	1·468448	6·7065	107·036
R V	1·47666	2·000164	6·6685	106·430
R VI	1·34887	1·837957	6·5900	105·177
R VII	1·74569	2·362320	6·6812	106·368
		Mean.....=	6·6646	106·368

In the calculation of these values (the weighings having been corrected), the atomic weights used were :—

Ag = 107·66
Cl = 35·37
N = 14·01
H = 1·00

The most cursory examination of these numbers shows that the variations are much greater than can be accounted for by the ordinary errors of experiment, nor are they attributable in any considerable degree to differences in the composition of the salt employed in the determinations. We found as a matter of fact that various causes were at work which interfered with the accuracy of the results.

In the first place, though we interposed several wash bottles, columns of moistened glass wool, or even collected and washed the hydrogen used in the reduction, small quantities of ammonium chloride were carried forward and lost, and this even when the hydrogen used for the reduction was passed very slowly. Secondly, there is little doubt that secondary decompositions occur during the process of reduction, and the combustion tubing used for the process was acted upon at the moderate temperatures employed to a greater extent than seemed likely to arise from the corrosive action of ammonium chloride. Amongst others, Seubert seems to have found the same difficulties in the determination of chlorine

in such decompositions, and thought the differences might be due to the india-rubber cork which he used, taking up hydrochloric acid. A remarkable passage occurs in the paper already referred to, in which Berzelius describes his experiments on palladium salts; we quote it, not only because it bears directly on this question, but also since it is particularly suggestive in view of recent investigations. Speaking of the palladammonium chloride which he had prepared, he describes it as a substance "welcher bei trockner Destillation zuerst ein wenig freies Ammoniak, dann Salzsaüre, Stickgas und endlich Salmiak giebt, während reines metallisches Palladium zur Hälfte seines Gewichts zurückbleibt. Dieses Salz ist dem *Mercurius præcipitatus albus* der Pharmaceuten analog, und besteht aus einem Atom Palladium chlorür und einem Doppelatome Ammoniak.

"Die Entstehung desselben gründet sich darauf, dass das Chlor des Chlorürs mit dem Ammoniak bildet: Chlorammonium, Stickgas und Salzsaüre."

As they stand, the results in Table II point to a value higher than 106 as the atomic weight of palladium, and so far are in agreement with the number obtained by Berzelius; but, as we shall see later, the value obtained from the palladium contained in the salt in experiments carried out with extreme care falls about one unit lower.

We have tried the distillation of the salt with pure caustic soda, so as to determine the ammonia given off and the chlorine remaining in the residue, but the reaction is incomplete, and neither this nor any of the other methods which we have thus far attempted have enabled us to check the results obtained in the experiments quoted above. Although the numbers found are sufficiently near to indicate that the salt has the composition which has been assigned to it, there can be no doubt of the desirability of an independent determination which shall afford more complete proof of its constancy of composition than is given in the succeeding experiments.

Determination of Palladium.

The tube in which the reduction had been performed was allowed to cool down to considerably below a red heat, and the hydrogen was then displaced by air. The boat now containing

the palladium was withdrawn and introduced into a porcelain tube, which was first exhausted and then exposed to a red heat in a charcoal furnace. Any gases evolved were drawn off by means of a Sprengel pump, the heating being continued for about two hours, at the end of which time no more gas appeared.

In order to avoid the possibility of alteration in the boat itself, it was wrapped in platinum foil, and in no case was the boat found to undergo loss of weight. Indeed, a boat which had been used for a number of determinations was not found to vary more than $\frac{1}{10}$ milligram. The palladium sintered together, forming a coherent mass resembling silver in appearance, although a little more dull. More than 20 determinations were made in this way in five series, two of which were with imperfectly purified material. The results of the *whole* of the determinations in the last three series, except those made with the earlier and later fractions, are given in the succeeding tables. Series A and B were preparations from palladium obtained by a method different from that used in Series C.

TABLE III.

Series A.

Denomination of fraction.	Weight of $Pd(NH_3Cl)_2$.	Weight of Pd.	Percentage of Pd.	Atomic weight, H = 1.
D II.....	1·890597	0·947995	50·1426	105·353
D III	1·874175	0·940271	50·1698	105·468

$Pd(NH_3Cl)_2$: Pd :: 3·764772 : 1·888266
Pd : O :: 6·60463 : 1·000000
Pd : H :: 105·410 : 1·000000

Series B.

Denomination of fraction.	Weight of $Pd(NH_3Cl)_2$.	Weight of Pd.	Percentage of Pd.	Atomic weight, H = 1.
E II	1·307076	0·654687	50·0878	105·123
E III	1·340045	0·673207	50·2376	105·754
E IV.....	1·905536	0·955950	50·1671	105·359
E V	1·685582	0·846472	50·2184	105·672

$Pd(NH_3Cl)_2$: Pd :: 6·238239 : 3·130316
Pd : O :: 6·6108 : 1·000000
Pd : H :: 105·508 : 1·000000

Series C.

Denomination of fraction.	Weight of $Pd(NH_3Cl)_2$.	Weight of Pd.	Percentage of Pd.	Atomic weight, H=1.
F II	1·691028	0·849120	50·2132	105·651
F III.....	2·112530	1·059690	50·1621	105·435
F IV.....	2·110653	1·057910	50·1224	105·267
F V	1·969100	0·988155	50·1838	105·523

$Pd(NH_3Cl)_2$: Pd : : 7·883311 : 3·954875

Pd : O : : 6·60767 : 1·000000

Pd : H : : 105·458 : 1·000000

Taking the mean of the three series, we have :—

Series A..... 105·410

,, B..... 105·508

,, C..... 105·458

Mean= 105·459

a value agreeing with Series C, on which we have reason to place the greatest reliance.

The Weighings.

The balance used was by Oertling, and had already been employed by one of us in the determination of the atomic weight of zirconium and also in other atomic weight determinations made at the Owens College.

The readings were made by means of a telescope, the image of the scale being reflected along the line of vision by mirrors.

The stability and sensibility of the instrument may be judged by the fact that in a series of weighings, extending over a fortnight, the extreme variation of the zero point did not exceed 0·3 of a division, whilst the displacement produced by the addition of a milligram was 11·1 divisions, and never varied more than 0·2 of a division.

We are of opinion that the readings may be relied upon to 0·25 of a division.

The weights used were an excellent set by Staudinger. They had several times been carefully compared, and in the calculations allowance was made for the slight inaccuracies which had been observed in them. The boat and palladium were enclosed in a stoppered bottle, and every precaution was taken to avoid the absorption or condensation of moisture during the operation of weighing.

The weighings have also been reduced to *vacuo*. For this purpose, the specific gravities of the substances used were determined, and in the case of palladium in the state in which it occurred after reduction, the specific gravity was found to be 11·12, that of the palladammonium chloride being 2·55.

In conclusion, as the atomic weights of the metals of the platinum group have now been all redetermined, it is not inappropriate to place them together for the sake of comparison :—

Ruthenium.	Rhodium.	Palladium.	Silver.
101·4	102·7	105·5	107·7
Osmium.	Iridium.	Platinum.	Gold.
190·3	192·5	194·3	196·8

The differences between the members of the same vertical series are thus :—

88·9	89·8	88·8	89·1

We propose to make further attempts to determine the chlorine in the palladammonium chloride and to ascertain the relation KCl : Pd in potassium palladious chloride. We, however, thought it desirable that the results already obtained should be published, and, indeed, we regard them as sufficient to establish the atomic weight, at any rate, with the degree of accuracy attainable in this group of elements. In conclusion, we must acknowledge valuable assistance from Mr. T. C. Moore, B.Sc., who carried out most of the preliminary investigations, but was unable to continue the work.

THE INFLUENCE OF DIFFERENT OXIDES ON THE DECOMPOSITION OF POTASSIUM CHLORATE.

By G. J. Fowler, M.Sc., *and* J. Grant.

(From the Journal of the Chemical Society.)

As several papers have recently appeared on this subject, it will be well to give some account of the origin and scope of the present work.

More than a year ago some experiments were made in this laboratory by J. Paul with a view to prepare pure oxygen from potassium chlorate. It was found that if the oxygen evolved was filtered through glass wool, before being collected over mercury, the latter remained quite clean on the surface when the gas was bubbled through it. Potassium chloride in considerable quantity was found in the glass wool, and no chlorine, or the merest trace, was evolved. It was found, however, that when silica or powdered glass was mixed with the chlorate, chlorine was given off in appreciable quantity. If, therefore, chlorine was given off at all on heating pure potassium chlorate, as some observers believed, its evolution appeared to be due to the action of a large surface of glass on the fused salt.

A few preliminary observations were then made on the effect of other substances, chiefly oxides, on the decomposition of potassium chlorate. The results obtained at that time seemed to be of sufficient interest to warrant a fuller inquiry. The work was therefore resumed later on, and a large number of experiments were made.

Since the beginning of the work, papers have been published by Hodgkinson and Lowndes, McLeod, and others, which have added considerable interest to the question. These experimenters have confined themselves chiefly to the action of manganese dioxide on potassium chlorate under different conditions. Hodgkinson and Lowndes have examined the effects of other oxides to some extent, and have anticipated some of the results recorded in this paper. Their conclusion with regard to the action of manganese dioxide on potassium chlorate is as follows (*Chem. News* lix, 63): "The manganese dioxide is alternately reduced and reoxidised by the potassium chlorate, but only in exceptional instances is the reoxidation complete. This reduction in a strongly oxidising atmosphere is probably due to the atomic attraction of the oxygen; the oxygen atoms in the chlorate and the dioxide pull at each other, and the force of attraction, combined with the decomposing effect of the temperature, is sufficient to break up both compounds." This theory, however, scarcely accounts for the evolution of chlorine which inevitably accompanies the oxygen.

McLeod (*Trans.*, 1889, lv, 184) comes to the conclusion that the manganese dioxide attacks the chlorate, forming potassium permanganate and liberating chlorine. The $KMnO_4$ decomposes by heat into K_2MnO_4, MnO_2, and O_2. The K_2MnO_4 is decomposed by fresh chlorine into KCl, MnO_2, and O_2, so that only a little chlorine is evolved and the manganese dioxide is constantly regenerated. If the evolution of chlorine is prevented by the addition of sodium carbonate, the oxygen is evolved at a much higher temperature. McLeod's theory of the action then is purely chemical.

Reference is made in McLeod's paper to work done by Baudrimont (*Journ. Pharm.* [4] xiv, 1871, 81, 161). This chemist has investigated the action of a number of oxides on potassium chlorate, notably manganese dioxide in various conditions, ferric oxide, and copper oxide, the temperature of evolution and the amount of chlorine evolved being noticed in each case. Baudrimont looks upon the action of manganese dioxide as being different from an ordinary chemical reaction, and speaks of it as an action by contact or presence, or as a catalytic action similar to the action of silver or platinum, silver oxide, or manganese dioxide on

hydrogen peroxide. It should be mentioned that in a discussion on Baudrimont's paper (*loc. cit.*, 130), Jungfleisch puts forward much the same view of the action as McLeod, and draws attention to the formation of potassium permanganate by projection of manganese dioxide into fused chlorate.

Warren (*Chem. News* lviii, 247) comes to the conclusion that only those oxides are active which are capable of forming higher oxides. He also believes that the evolution of chlorine may be due to the formation of a manganate in the case of manganese dioxide.

Veley (*Phil. Trans.*, 1888 [1], 271) draws attention to the action of finely-divided particles in promoting the evolution of gases from liquids, and considers the action of manganese dioxide upon potassium chlorate to be due (1) to the finely-divided state of the manganese dioxide; (2) to the chemical interaction between it and the chlorate.

Finally, Spring and Prost (*Bull. Soc. Chim.*, 1889, 340-342) have heated the chlorates of several metals in porcelain and platinum vessels in presence of carbon dioxide, silica, and phosphorus pentoxide.

They consider that the evolution of oxygen is an indirect phenomenon, the chlorate first splitting up into $M_2O+Cl_2O_5$. The Cl_2O_5 yields Cl_2+O_5 when we have $M_2O+Cl_2=2MCl+O$. The reaction is incomplete if the chlorine is carried away by the violence of the reaction, or if the base forms a salt on which the chlorine has no action. A strong base (K_2O for example) may oxidise the Cl_2O_5, a perchlorate being formed.

From the foregoing summary of the work which has been done in this direction, it is sufficiently evident that no simple interpretation is to be expected of the reaction which takes place during the decomposition of potassium chlorate, and its character is manifestly largely influenced by the presence of other bodies.

Our object in this work has been to examine systematically the influence of the chief metallic oxides and certain unstable salts on the decomposition of potassium chlorate. We have determined in each case the temperature at which oxygen is evolved, the amount of chlorine given off, and the composition of the residue after heating. These results varied with the acid or basic character of the oxide, with its physical condition, and with the

relative masses of oxide and chlorate, and by comparison of the data thus obtained we have sought to arrive at a general explanation of the action, not only of manganese dioxide, but of other oxides which are effective in promoting the decomposition of potassium chlorate (either with or without evolution of oxygen).

Description of Apparatus.

The apparatus employed consisted of a sheet-iron cylinder, acting as an air bath, 9 inches in height and 7½ in diameter. The lid was loose, and the bottom riveted on; in the movable lid were two circular holes at equal distances from the sides and centre. One of these was for the air thermometer, a small glass bulb and tube of 30 c.c. capacity attached to a glass tube bent twice at right angles, and terminating in a manometer tube containing mercury. This was graduated by a mercurial thermometer up to 280°; the higher temperatures being calculated afterwards. It is probable that these values are somewhat too high; the numbers, however, are comparable among themselves, which is sufficient for the object we had in view. The other aperture in the lid admitted the chlorate bulb, to which was attached, by thick india-rubber, a long glass delivery tube, the gases being passed before collection through a solution of potassium iodide. Both bulbs reached to the centre of the cylinder. Two large Bunsen lamps were used, the flames of which surrounded the whole apparatus. Of course all care was taken to insure that the same conditions, as nearly as possible, obtained throughout the series of experiments, as to heating arrangements, strength of potassium iodide solution, character of potassium chlorate used, &c. Indeed, with regard to the latter point, more than a pound of potassium chlorate was freed from chloride and other impurities, and finally recrystallised; this served for the whole of the series of experiments.

In the following experiments, statements regarding the amount of chlorine given off are expressed approximately in terms of the quantity evolved when one part of manganese dioxide is mixed with three parts of potassium chlorate. Exact quantitative measurements were not made, a rough comparison appearing sufficient for our purpose.

Oxides of Antimony, Tungsten, Uranium, and Vanadium.

The results of experiments with these oxides are summarised in the following table. The temperatures given in these and other experiments are those at which a moderately brisk evolution of oxygen began to take place.

I. No. of expt.	II. Formula of oxide.	III. Relative masses of oxide and chlorate.	IV. Temperature.	V. Remarks.
63	Sb_2O_5	1 : 2	340°	Large quantity of chlorine in each case. On treating residue with hot water and filtering, potassium antimonate found in filtrate.
64	,,	2 : 1	430	
65	,,	3 : 1	440	
92	U_3O_8	1 : 2	390	Large quantity of chlorine evolved. Reddish-yellow residue dissolving to yellow solution of potassium uranate.
93	,,	2 : 1	390	
110	WO_3	1 : 2	250	Not so much chlorine as with V_2O_5. Potassium tungstate found in residue.
109	V_2O_5	1 : 2	150—170	Large quantity of chlorine. Red-coloured residue soluble in water to golden-coloured solution of potassium metavanadate.

It will be noticed that the temperature of evolution is lower, the more acid the oxide.

It may be mentioned here that the slightest trace of an acid (such as nitric) is sufficient to break up the chlorate at a low temperature; for instance, bismuth sesquioxide has little action on potassium chlorate. From a mixture of 2 grams chlorate with 0·75 Bi_2O_3 and 0·25 $Bi(NO_3)_3$, oxygen is evolved quickly at 300°, together with chlorine. The action of nitric acid on the chlorate will of course be complicated.

Again, titanium dioxide containing a slight trace of sulphuric acid brings off the oxygen at a low temperature, whilst the pure oxide has but little action.

Oxides of Aluminium, Silicon, and Tin.

I.	II.	III.	IV.	V.
20	Al_2O_3	1 : 2	400°	4 units chlorine evolved.
42	SiO_2	1 : 2	400	4 units chlorine.
95	SnO_2	1 : 2	470	1 unit chlorine.

It will be seen that alumina and silica agree very closely in their properties (compare Mills, "On the Action of Oxides on Salts," *Journ. Chem. Soc.*, 1879, ii, 336). On extracting the residue, after heating, with water, an alkaline solution was obtained in both cases.

In the case of tin oxide, only a very small trace of tin could be dissolved out on treating the bulb contents with water, and the solution was not alkaline. Tin oxide, however, as is seen from the table, is not specially active. In this case the tin oxide used was prepared in the dry way, as it was found difficult to free the precipitated oxide from nitric acid. The greater activity of the precipitated oxide appeared to be partly due to this cause; after ignition it is not so active.

We may conclude that these oxides act upon the chlorate in the same manner as those of the last class. They are less active, however, according as the attraction between the oxide and K_2O is weaker.

Sesquioxides of Chromium, Antimony, and Arsenic.

With regard to these oxides there is not much further to be said. With all of them oxidation takes place, accompanied in the case of antimony and arsenic oxides by incandescence. Chromate, antimonate, and arsenate of potassium are formed. Chlorine is evolved in each reaction, most copiously in that produced by chromium sesquioxide.

Oxides of Manganese, Iron, Nickel, Cobalt, and Copper.

The monoxides of iron, nickel, cobalt, and manganese, and the suboxides of copper, are oxidised by the chlorate with explosive rapidity, a great rise of temperature taking place.

The reaction which is brought about by manganese dioxide has already been discussed. We may mention that at the outset of our experiments we noticed the pink colour of the permanganate produced when a trace of manganese dioxide is fused with the chlorate.

What takes place in the case of the higher oxides of iron, cobalt, nickel, and copper, it is difficult directly to determine. The close agreement of their mode of action with that of manganese dioxide seems to point to an analogous reaction taking place. Higher oxides would seem to be formed in all cases; these combine with the K_2O to form unstable compounds which are broken up like the permanganate in the case of manganese dioxide.

The following table gives the results of some of the experiments made with *manganese dioxide*:—

I.	II.	III.	IV.	Cl evolved.	Remarks.
2	MnO_2.	1 : 3	370°	unit	With 2 and 3 there was a rush of gas.
3	„	1 : 4	330	less	
6	„	1 : 6	340	(same as 3)	In 6, 7, and 8 the same oxide was used. Powdered pyrolusite was made use of.
7	„	1 : 6	340	„	
8	„	1 : 6	340	„	
4	„	1 : 8	360	(less than above)	

The results show that the temperature of initial action is altered to some extent by variations in the ratio of oxide to chlorate. There is a certain ratio, however, which produces the most regular evolution of oxygen, this being one part manganese dioxide to six parts chlorate, with which there is a rapid and regular evolution at 340° to 360°. With smaller quantities of chlorate in proportion to the manganese, there is apt to be a rush of gas.

If the temperature be quickly raised, chlorine comes off more abundantly (*see* Warren, *Chem. News* lviii, p. 247, Nov., 1888), apparently because the equilibrium is disturbed, there not being sufficient time for the chlorine to decompose the manganate.

The following are the results of some of the experiments made with *ferric oxide* :—

I.	II.	III.	IV.	Units of Cl evolved.	Remarks.
79	Fe_2O_3	1 : 6	380°	$3\frac{1}{2}$	Very rapid evolution.
10	$Fe_2(OH)_6$	1 : 2	440°	2	Rapid evolution.
12	Fe_2O_3	2 : 1	280°	less	,, ,,
13	$Fe_2(OH)_6$	4 : 1	380°	much less	Steady evolution, less rapid

With ferric oxide more chlorine is evolved, and under certain conditions the oxygen comes off at a lower temperature than with manganese dioxide. In experiment 12, where this is the case, the oxide had been previously used ; this seems to improve rather than diminish its activity.

The relative masses of oxide and chlorate and the presence of water of hydration both have considerable influence on the temperature of evolution, and on the quantity of chlorine given off. If sodium carbonate is added to the mixture of ferric oxide and chlorate, the temperature at which the oxygen is evolved is greatly increased as in the case of manganese dioxide.

The *sesquioxides of cobalt and nickel* resemble each other in their action very closely. The temperature of evolution is lower than with manganese dioxide and ferric oxide. With one part of Co_2O_3 to two parts of chlorate, a rush of gas took place at 250°. Less chlorine is given off than is the case with ferric oxide.

With *cupric oxide* all the gas appears to come off with a rush at one particular temperature. Very little chlorine is evolved. In experiment 32, for example, one part of cupric oxide, previously used, was mixed with two of chlorate. At 350° no gas was coming over ; at 360° it all came over with a rush, very little chlorine being evolved.

Baudrimont (*loc. cit.*) noticed that with cupric oxide the evolution of oxygen is accompanied by a rise of temperature, which seems to point to the breaking up of some compound formed with absorption of heat. Sodium carbonate in this case also checks the evolution of oxygen.

Oxides of Mercury, Silver, Lead, Barium, and Calcium.

Some interesting results were obtained with the above oxides. After heating each of them with potassium chlorate for a considerable time at a high temperature (about 500°), no gas (or only a mere trace) was evolved. The contents of the heating bulb were treated with boiling water, filtered, and both residue and filtrate examined. The filtrate in all cases contained potassium perchlorate.

Mercuric Oxide.—On heating mercuric oxide alone at 360° (in mercury vapour), it underwent no change. On mixing it with chlorate, however, and heating at the same temperature, a sublimate of metallic mercury was formed on the sides of the heating tube, and there was a slight loss of oxygen from the mixture. On dissolving the residue in water and filtering, potassium perchlorate was found in solution, and on passing sulphuretted hydrogen, sulphide of mercury was precipitated, showing that some mercuric chloride had been formed in the reaction.

Oxide of Silver.—Although the mixture of silver oxide and chlorate was heated for considerably over an hour at a temperature far above that at which silver oxide decomposes (270°—280°), no evolution of gas took place. On treating the contents of the bulb with hot water and filtering, pure silver was left behind, and the filtrate contained large quantities of potassium perchlorate.

Peroxide of Lead.—After the first heating with chlorate, the washed residue is composed partly of the dioxide and partly of red lead. The second heating with fresh chlorate did not complete the conversion, but on a third trial the whole of the dioxide was transformed into red lead. Potassium perchlorate was formed in each case. At a very much higher temperature the Pb_3O_4 became reduced to PbO. A trace of chlorine was evolved in the above cases. If lead oxide is heated with excess of chlorate to a moderate temperature, the peroxide is formed, also potassium perchlorate, by a back reaction.

Oxides of Barium and Calcium.—When barium dioxide is heated with chlorate, a considerable quantity of potassium perchlorate is obtained; the barium dioxide is reduced. The monoxides of barium and calcium are oxidised to the peroxides, potassium perchlorate being still formed by a reverse action, but in smaller

quantity than when the dioxide is used to begin with. In the case of barium dioxide, the temperature employed influences the quantity of perchlorate formed. Thus at 350° (mercury vapour) more perchlorate is formed than at 448° (sulphur vapour).

The influence of certain salts on the decomposition of the chlorate may be mentioned here as being of interest in connection with the foregoing experiments.

Permanganates of Potassium and Silver.

I.	II.	III.	IV.	V.	Remarks.
66	$KMnO_4$	1 : 2	370°	nil	Very rapid evolution.
67	,,	2 : 1	360	unit	Rapid evolution.
69	$AgMnO_4$	1 : 2	500	trace	Very rapid evolution.
70	,,	2 : 1	490	trace	Rapid evolution.

The explanation of the action of the permanganates of potassium and silver is, no doubt, that at the high temperature the permanganates decompose, according to the following equations :—

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2,$$
$$AgMnO_4 = Ag + MnO_2 + O_2.$$

The manganese dioxide then acts in the manner already described, but no chlorine is evolved, owing to its combination with potassium and silver.

Potassium Dichromate.

When potassium dichromate and potassium chlorate are heated together, the mixture first fuses, then gives off oxygen, without chlorine, accompanied by a great deal of frothing. The dichromate appears to suffer no change, except at a very high temperature, when a certain amount of chromate and perchlorate of potassium is obtained.

Potassium Nitrate.

On heating a mixture of potassium nitrate and chlorate, both oxygen and chlorine came over slowly. When the temperature is raised to dull redness, gas was evolved rapidly with much frothing. The residue left, after heating at this temperature for some time, contained a considerable amount of potassium nitrite.

From the foregoing experiments, it seems probable that, in all the cases considered, the influence of the oxide upon the decomposition of the chlorate is largely chemical, although, in some cases, physical causes help to bring about the result (Veley, *loc. cit.*).

The mode in which the chemical action proceeds depends upon several factors :

The affinity of the oxide for K_2O
" " " O
" " " $O+K_2O$
The affinity of the chlorate for O.

It will be readily seen that the problem is a complicated one. It is very difficult in many cases to determine the exact course of the reaction, as more than one change may take place at once.

The above generalisations are illustrated by the following summary of our results :—

1. Acid oxides, such as V_2O_5, U_3O_8, WO_3, evolve oxygen at a reduced temperature, a metavanadate, uranate, or tungstate being formed. Chlorine is evolved, in these cases, in *large* quantity. The whole of the oxygen of the chlorate is not evolved, the compound of K_2O with the oxide not being decomposed by heat or by chlorine. Here it is evident that a leading factor in bringing about the reaction is the affinity of the oxide for K_2O.

2. Alumina probably acts like the above oxides, but less energetically, the attraction between the K_2O and Al_2O_3 not being so great.

3. In the case of chromium sesquioxide the oxygen comes off at a reduced temperature, accompanied by chlorine. The reaction would seem to be brought about here by the affinity of the Cr_2O_3 for O, and the affinity of the CrO_3 thus formed for K_2O.

4. In the case of the sesquioxides of iron, cobalt, and nickel, cupric oxide, and manganese dioxide, oxygen is evolved at a comparatively low temperature, accompanied by only a little chlorine; the oxide is left but little altered at the end of the experiment. Here it is probable that an unstable equilibrium is produced, resulting in the decomposition of the chlorate.

Accepting McLeod's theory of the action of manganese dioxide (which is fully in harmony with our own results), it would seem that manganese dioxide acts, to begin with, by reason of its

affinity for oxygen and the affinity of the higher oxide thus formed for K_2O. The permanganate first formed, however, is unstable (here there is a difference between the oxides of this class and those of the preceding); it splits up on heating into $K_2MnO_4 + MnO_2 + O_2$. *The* K_2MnO_4 *is decomposed by the fresh chlorine which is liberated* (Spring and Prost, *loc. cit.*) into KCl and MnO_2, which is thus regenerated. The addition of sodium carbonate retards the evolution of oxygen, probably because the manganate is thereby rendered more stable.

The action of the other oxides of this class can, we believe, be explained in a manner similar to that of manganese dioxide.

5. The oxides of barium, calcium, and lead cause no evolution of oxygen when heated with chlorate, but the latter breaks up below its normal temperature of decomposition, potassium chloride and a peroxide being formed. Here the affinity of the oxide for oxygen brings about the change.

6. On the other hand, potassium chlorate may act as a reducing agent in the presence of such oxides as silver oxide and the peroxides of barium and lead, a perchlorate being formed. No oxygen is evolved. Here the reaction is brought about by the affinity of the chlorate for oxygen. In the case of the oxides of calcium, barium, and lead, the extent to which the chlorate is oxidised or reduced evidently depends on the masses of the reacting substances.

7. We have found that water of hydration diminishes the activity of an oxide.

8. The physical condition of the oxide is of influence (*see* Wright and Luff, *J. Chem. Soc.*, 1878, p. 1). Copper oxide, prepared in the dry way, is almost inactive.

9. Certain bodies, which apparently undergo no chemical change whatever, yet assist the reaction, as powdered glass, sand, kaolin.

In this case the action of fine particles (*see* Veley, *loc. cit.*) is of influence, as it was found that the above-mentioned bodies lost their activity to a large extent when the more finely-divided particles were washed out.

10. Certain oxides, such as those of zinc and magnesium, are completely inactive.

SOME EXPERIMENTS ON THE VOLATILITY OF ANTIMONY AND ARSENIC IN DIFFERENT GASES.

By G. J. Fowler, M.Sc., *and* L. St. G. Byne.

WHEN testing for arsenic and antimony by Marsh's method, it was frequently noticed that if the mirror produced by heating the tube attached to the hydrogen evolution flask was slight, it quickly disappeared on removal of the flame. It seemed possible that this was due to a re-combination of the arsenic or antimony with the hydrogen, a direct union comparable to the formation of hydrogen sulphide by passing hydrogen over heated sulphur.

The following experiments were made to determine whether direct combination does or does not take place between hydrogen and arsenic or antimony under the above conditions. Towards one end of each of a number of hard glass tubes (about 5 mms. in diameter and 30 cms. long) a good mirror of either antimony or arsenic was deposited. A tube containing an antimony mirror was connected (by the end nearest the mirror) to a flask evolving hydrogen (previously tested for freedom from antimony or arsenic). The mirror was heated, and also a portion of the tube about six inches further away from the hydrogen apparatus. A faint mirror was formed at the second point of heating, a stain being also produced on a porcelain lid held in the flame of the escaping hydrogen. On heating this stain with a drop of ammonium sulphide, the orange sulphide of antimony was formed. This stain was only obtained when the mirror on the tube was heated, and ceased also after a time when the mirror appeared to become fused into the glass.

This experiment favoured the supposition that direct combination had taken place between the hydrogen and antimony, the temperature of combination being near to the temperature of decomposition of the hydride formed. Similar experiments with other gases point, however, to its being entirely a mechanical phenomenon. In dry carbon dioxide a slight film of oxide of antimony was deposited close to the second flame. The same result took place in a current of carbon monoxide which had passed through alkaline pyrogallate and strong sulphuric acid. A stain of antimony was produced on a porcelain lid held in the flame of carbonic oxide, burning at the end of the tube.

A mirror of arsenic was heated in a current of hydrogen and also of carbon dioxide, and similar results were obtained to those already described. The second deposit, however, was larger in the case of arsenic. It was also noted that a faint deposition of arsenic took place all along the tube between the two points of heating, the deposit appearing to accumulate in front of the second flame. This was especially noticeable on cooling the space between the two points of heating. This phenomenon was characteristic of other volatile substances, *e.g.*, ammonium chloride, arsenic, sesquioxide, and benzoic acid similarly heated in a stream of carbon dioxide. In the case of antimony and antimony sesquioxide, however, this thin film between the two points of heating could not be discovered. It is probable that the deposition takes place in a similar manner in all these cases; but the amount of deposit being smaller in the case of antimony, the intermediate film cannot be seen.

Further experiments pointing to the purely mechanical nature of the phenomenon are as follows: A tube similar to those already described was bent at one end into a U, and an arsenic mirror deposited in the bend; a current of pure hydrogen was passed through the tube while the U and the contained mirror were gradually heated in a bath of calcium chloride. A portion of the tube beyond the U was heated in a Bunsen flame. When the bath reached a temperature between 160° and 170° C., a deposit was formed just beyond the red-hot spot. This may be taken roughly to represent the temperature at which arsenic volatilises in a stream of hydrogen. On passing the hydrogen from the gradually-heated tube into a strong solution of silver nitrate for

some time, and testing carefully afterwards for arsenious acid, none, or the merest trace, could be found, showing that arsenic hydride was not formed under these conditions.

Finally, the mirrors were heated in a stream of pure nitrogen, obtained by the inter-action of copper, ammonia solution, and air, and subsequent washing of the gas successively in dilute sulphuric acid, chromous chloride, caustic soda, and strong sulphuric acid. Precisely similar results were obtained on heating a second portion of the tube. A black deposit of antimony took place, and also of arsenic, and in the latter case the escaping gas possessed a strong garlic odour.

Under the conditions of these experiments it may be therefore concluded that no direct combination of hydrogen with arsenic or antimony occurs.

THE BEHAVIOUR OF THE MORE STABLE OXIDES AT HIGH TEMPERATURES: CUPRIC OXIDE.

By G. H. Bailey, D.Sc., Ph.D., *and* W. B. Hopkins.

(From the Journal of the Chemical Society.)

FROM a number of statements which occur in works on metallurgy, and observations made on changes which take place when cupric oxide is exposed to high temperatures, it is quite evident that under such circumstances there is a loss of oxygen. In most cases the observer has contented himself with stating that the product obtained is cuprous oxide, without giving the grounds on which this conclusion is based. On the other hand, however, there exist records of experiments in which the conditions of working and the products obtained are carefully described, and it will be of interest in regard to the results arrived at by us to give a brief *résumé* of the investigations which have been made on the lower oxides of copper. The earliest of these appeared in 1845 (*Compt. Rend.* xviii, 658), when Favre and Maumené, by heating cupric oxide at the temperature of melting copper, obtained a dark-coloured substance having the composition Cu_3O_3. Although oxygen was given off freely at this temperature, it was taken up again at a cherry-red heat.

Vogel and Reischauer (*Jahresb. Chem.*, 1859, 216) obtained cuprous oxide by heating cupric oxide, and Marchand (*J. pr. Chem.* xx, 505) found that on exposing cupric oxide in a muffle for half an hour at a white heat, and then for eight hours at a dull red heat, the product remaining had the composition Cu_2O.

Without mentioning the many well-known reactions in which cuprous oxide is formed, it may be remarked that Gladstone and

Tribe (*Chem. News* xxv, 193) observed it as a yellow coating when a copper-silver couple was placed in a solution of nitrate of copper. The hydrated oxides prepared by Siewert (*Zeitschrift für Chemie*, 1866, 363), $Cu_2O_2.2H_2O$ and $Cu_4O_5.5H_2O$, and the tetrantoxide, Cu_4O (hydrated), of Rose (*Ann. Chim. Phys.* cxx, 1) must also be mentioned.

With the exception of Rose's oxide, all these may be classified on the assumption that they are derivatives of cuprous and cupric oxides :—

Rose's oxide	Cu_4O.
Cuprous oxide	Cu_2O (and cuprite).
Favre and Maumené's oxide ...	$2Cu_2O,CuO$.
Siewert's oxide (a)	$Cu_2O,CuO,2H_2O$.
,, ,, (b)	$Cu_2O,2CuO,5H_2O$.

That cuprous oxide is obtained when cupric oxide is exposed in an oxidising atmosphere at a moderate temperature seems pretty conclusively shown.

Our object at the outset of this investigation was to examine whether cuprous oxide is the ultimate product when cupric oxide is exposed to high temperatures, or whether by using higher temperatures a further loss of oxygen took place.

Method of Experiment.

Finely powdered cupric oxide was exposed to a white heat in a Fletcher injector furnace, care being taken to preserve an oxidising atmosphere during the course of the experiment. At the temperature used, fire-clay crucibles were attacked by the copper oxide with the formation of a fusible slag, so that in most of the experiments recorded in this paper recourse was had to lime crucibles. As the temperature rose the oxide fused, and then bubbles of gas were seen to come off freely, the heating being continued—at least, so long as there appeared to be any gas given off.

On cooling, a yellowish-red mass was obtained hard enough to scratch glass quite easily, and having the sp. gr. 3·81. A thin film of black oxide with which it was coated (and which evidently formed during the process of cooling down) was removed, though, indeed, it was so thin that it could hardly have affected the analytical determinations.

Analysis of Product.

The finely powdered oxide was analysed by reduction in a stream of dry hydrogen, the water which was formed being absorbed in a calcium chloride tube in the usual manner, whilst the weight of copper remaining in the boat afforded a check on the results.

Several experiments were made, the time during which the oxide was exposed varying from one to three hours. In all cases the product obtained had the same properties and composition, the percentage of oxygen being always found to fall between 7 and 8 per cent.

A larger quantity was now prepared, the central portion of which was taken for analysis, so as to be sure that no particles of lime had found their way into it. The results of the analysis were as follow :—

Substance taken	0·615	gram.
Water obtained	0·0535	,,
Copper ,, ...	0·568	,,
Copper (by difference)	0·5655	,,

The percentage composition calculated from these numbers agrees well with that required for Cu_3O:—

	Found.	Calculated.
Copper	92·36	92·23
Oxygen.....	7·73	7·77

For the sake of comparison, it may be stated that the oxides Cu_2O and Cu_4O contain 11·22 and 5·94 per cent. of oxygen respectively.

Although every care was taken to preserve an oxidising atmosphere in the furnace, further proof was deemed desirable that the loss of oxygen was not due to reducing action of the flame. A piece of hard lime was therefore hollowed out, and in this the oxide was exposed to the oxy-hydrogen or rather oxy-coal-gas flame, in such a way that only the extreme point of the oxidising flame was allowed to play upon it. Fusion took place as before, and gas was observed to be given off; when the evolution of gas had ceased the mass was allowed to cool. The product in all respects resembled that obtained in the Fletcher furnace, and where it came in contact with the lime there was formed a bright

vermilion coating which consisted of lime and a lower oxide of copper, but which was not further examined. The results of two determinations were:—

	I.	II.
Substance taken	0·564	0·494
Water obtained	0·045	0·042
Copper ,,	0·524	0·457
Copper (by difference)	0·524	0·456

We have thus:—

	I.	II.	Calculated.
Copper	92·90	92·51	92·23
Oxygen	7·09	7·55	7·77

The results of the analysis show that the product obtained at the higher temperature is substantially the same as that obtained at the lower, and that it therefore maintains a constant composition within a fairly wide range of temperature, the limits of which we consider are approximately 1500° and 2000° C.; at any rate platinum readily fuses at the higher temperature used. From this it appears that as the oxides of smaller stability give up oxygen at moderate temperatures, so the more stable oxides, such as oxide of copper, are transformed into lower oxides at higher temperatures without the intervention of any reducing agent. Furthermore, as the evidence of several experimenters seems conclusive that cuprous oxide is obtained when a dull-red heat is used, there is—especially if we include Rose's oxide—an indication that the points of stability occur at definite stages in the process of transformation into the lower oxide, since we have the series Cu_4O, Cu_3O, Cu_2O, CuO. And although our object in this research is rather to accentuate the behaviour of oxides when exposed to high temperatures, it does seem as though sufficient evidence existed for the assumption that Cu_3O may be regarded as a definite oxide of copper, especially when its properties as given below are taken into consideration.

Action of Reagents on Cu_3O.

Even when reduced to the finest state of division in an agate mortar, the oxide is entirely unacted on by concentrated (or dilute) mineral acids; even aqua regia and boiling concentrated sulphuric acid are without action. Hydrofluoric acid, however, slowly

attacks it with the formation of a blue, crystalline fluoride of copper which has not been further examined. The only method by which we were able to bring the oxide into solution for the purpose of confirming the analysis by an entirely different process, was to fuse it with caustic potash, in which it dissolved with a blue colour, and from which it separated again on the addition of water in flocculent, brown particles. This, dissolved in sulphuric acid and titrated with potassium permanganate, was found to contain 9·8 per cent. of oxygen, a result falling about midway between Cu_3O and Cu_2O; it was, however, to be expected that some oxidation would take place in the process of fusion and extraction with water; in spite of this, however, the product contained less oxygen than Cu_2O.

It would be interesting to analyse a number of samples of native cuprite in order to see if they yielded any indication of exposure to temperatures such as were used in these experiments. We are continuing the work and proceeding with the examination of other oxides, and have indeed already obtained evidence that litharge, sesquioxide of bismuth, and vanadic acid lose oxygen in the same way as cupric oxide.

A PEROXIDE OF TITANIUM.

By G. H. Bailey, D.Sc., Ph.D., *and* E. Dowson.

WHEN hydrogen peroxide is added to a solution of titanic acid in dilute sulphuric acid a reddish-yellow colouration is produced, the intensity of which is proportional to the amount of hydrogen peroxide added or to the amount of titanic acid present in the solution (*Weller. Ber.* xv, 2592). Piccini has further shown that when such a solution, which he prepared, however, by the addition of peroxide of barium, was treated with alcoholic potash, a yellow precipitate was obtained. The composition of this precipitate varied between Ti_2O_5 and Ti_5O_{11}, and his analyses gave evidence of the series :—

$$4\ TiO_2\ .\ TiO_3 = Ti_5O_{11}$$
$$3\ TiO_2\ .\ TiO_3 = Ti_4O_9$$
$$2\ TiO_2\ .\ TiO_3 = Ti_3O_7$$
$$TiO_2\ .\ TiO_3 = Ti_2O_5$$

He was also led to conclude from an examination of the reddish-yellow liquid that the oxide TiO_3 existed in the solution.

Some time ago in this laboratory we repeated the experiments, working both with freshly precipitated peroxide of barium and with hydrogen peroxide. A deep red liquid was obtained which resembled in appearance a solution of chromic acid. This was diluted with twice its volume of alcohol, and then a strong solution of potash in alcohol was added, the precipitation being conducted in three or four fractions and filtered off separately. The precipitates were of a yellow colour, the middle fractions being of a bright orange. When treated immediately, the precipitate so obtained was soluble in water, and it was therefore washed several times with alcohol to remove water and any excess of hydrogen peroxide,

and finally the alcohol was removed by washing with ether. The analysis was made by two different methods. Either the moist oxide was distilled with hydrochloric acid and the chlorine liberated was measured by ascertaining the amount of iodine which it liberated from a solution of potassium iodide, or, the oxide was dissolved in water and treated with potassium permanganate to determine the additional oxygen; in both cases the titanic acid was estimated by precipitation with ammonia. The results obtained are given in the following table; water of hydration being neglected :—

	TiO_2.	O.	
(1.)	·0105	·0021	grams.
(2.)	·0150	·00296	,,
(3.)	·0160	·0033	,,
(4.)*	·0299	·00422	,,
(5.)*	·0233	·00397	,,

The percentage composition of the products calculated from these results was :—

	(1.)	(2.)	(3.)	(4.)	(5.)
TiO_2	83·33	83·52	82·91	87·63	85·44
O	16·66	16·48	17·09	12·37	14·56

Calculating for Ti_2O_5 and TiO_3 we obtain—

	For Ti_2O_5.	For TiO_3.
TiO_2	90·91	83·33
O	9·09	16·66

The oxide had therefore the composition TiO_3. Thus, titanium, like other members of this group, forms a tolerably stable peroxide which is soluble† in water and gives rise to a deep red solution, and in these respects exhibits analogies to chromium.

All the members of this family have yielded trioxides, and the question naturally arises, will carbon also yield a trioxide? At the suggestion of Mr. R. S. Dale, barium peroxide was suspended in water and the water charged with carbon dioxide under high pressure, and left in this state for some days. On opening the bottles it was found that the pressure had diminished considerably. Moreover, the clear liquid decanted off and evapo-

* No. 4 was air-dried and No. 5 was partially dried, the remainder being analysed in the moist state.

† An insoluble modification is formed if the precipitate is allowed to stand

rated in vacuo or left to stand for several weeks deposited crystals which differed in their reactions from barium carbonate, whilst they also liberated iodine from a solution of potassium iodide. The reaction was not due to free hydrogen peroxide, for no reaction occurred until the liquid was warmed.

The observations point to the existence of such a body as $BaCO_4$, though as yet the crystals have not been obtained in sufficient quantity to establish this by means of a gravimetric analysis.

Of course $BaCO_4$ may be $BaO_2 . CO_2$, or it may be $BaO . CO_3$. It may be remarked also that the same interpretation is possible in the case of the peroxides of this group which are only stable in the hydrated condition, and may be equally $RO_3 . 3H_2O$ or $RO_2 . H_2O_2 . 2H_2O$. To take the case of zirconia as an instance, the oxides are—

$$Zr. O_2 . 2H_2O$$
$$Zr. O_3 . 3H_2O$$

and the latter may equally have the constitution—

$$Zr. O_2 . H_2O_2 . 2H_2O.$$

Note.—This work was carried out with a view to the isolation of the oxide, whose presence in solution had been suspected by Piccini. It was afterwards found that Classen (*Ber.* xxi, 370) had just previously obtained an oxide evidently identical with ours. This paper therefore serves to confirm his results, and gives some additional information with regard to the preparation and properties of titanium peroxide.

PERSULPHIDE OF LEAD.

By G. J. Fowler, M.Sc., *and* Ernest Bury.

SOME time ago, when testing for lead, a solution of ammonium sulphide was used which had been kept for some time, and which contained excess of sulphur. A bright hæmatite red precipitate was obtained, which soon took the appearance of ferric hydrate, and finally changed to ordinary black lead sulphide.

On referring to Watts' and other dictionaries, we found that a similar substance had been observed by Berzelius, and considered by him to be pentasulphide of lead. As we could find no other information about this body, it seemed of interest to examine it further.

The substance, as already remarked, rapidly loses its colour, and yields ordinary black sulphide of lead; it was, therefore, not possible to obtain a sample in the dry state for analysis. The change is not due to the action of the air, as on filtering the substance in an atmosphere of coal gas, it took place quite as rapidly. However, if the precautions described are taken, it is possible to keep the substance nearly in its original condition during the time necessary to rapidly wash it by decantation.

The solution of ammonium sulphide is made by boiling the ordinary sulphide with excess of sulphur for about twenty minutes or half an hour. The solution obtained is filtered and then diluted considerably, and immediately, before sulphur begins to separate out, added to an ice-cold dilute solution of lead acetate. The latter should be kept in excess. The red precipitate obtained thus is thoroughly washed by decantation, and the supernatant liquid poured off as completely as possible. The precipitate is then treated in an Erlenmeyer flask with fuming nitric acid, and warmed on a

water bath till completely dissolved. After removal of excess of nitric acid by evaporation, the sulphate of lead separates out on the addition of pure alcohol and water. This was estimated on a weighed filter after drying at 120°. The sulphuric acid remaining in the filtrate was precipitated, after boiling off the alcohol, by barium chloride, and the barium sulphate was dried and weighed.

The amount of sulphur in the lead sulphate and barium sulphate respectively indicates the ratio that exists between the sulphur in the normal sulphide and the additional sulphur required to form the persulphide.

The following results were obtained :—

Sample A (Bright Red).

$PbSO_4$ obtained = ·4865 gram.
$BaSO_4$,, = ·3915 ,,

Ratio = 1 : 1·07.

Hence

Formula = PbS_2.

Sample B (Darker than A).

Wt. of $PbSO_4$ obtained = ·1545.
,, $BaSO_4$,, = ·2790.

Ratio = 1 : 2·3.

Hence

Formula of substance = Pb_3S_{10}.

Sample C (Similar to B).

Wt. of $PbSO_4$ obtained = ·1750.
,, $BaSO_4$,, = ·3460.

Ratio = 1 : 2·7.
Formula = Pb_3S_{11}.

Sample D (Bright Red).

Wt. of $PbSO_4$ obtained = ·5235.
,, $BaSO_4$,, = ·5540.

Ratio = 1 : 1·3.
Formula = Pb_3S_7.

In no case, it will be seen, does the amount of sulphur found correspond with the formula PbS_5, and as samples A and B had

certainly best preserved their appearance, it seems that the red precipitate consists of lead disulphide. The existence of an unstable disulphide of lead analogous to the comparatively unstable dioxide of lead is probable.

The precise reaction by which it is formed from polysulphide of ammonium is not at once apparent. We propose to investigate this point, and to determine, if possible, with more exactitude the composition of the precipitate formed in this and in other cases.

It may be mentioned that in some experiments which are being conducted in this laboratory on hydrogen persulphide (which, according to Sabatier*, has the formula H_2S_2), a much larger yield of this substance was obtained from a solution of polysulphide of lime containing excess of sulphur, than from a carefully prepared solution of potassium disulphide. The latter solution added to a lead salt gave at once a black precipitate.

The above facts would point to the conclusion that the reactions by which the persulphides of lead and hydrogen are formed are not simple double decompositions.

* *Comptes Rendus*, 100, 1585.

SOME EXPERIMENTS WITH SILVER PERMANGANATE.

By G. J. Fowler.

THESE experiments were undertaken in order to discover whether, on treating silver permanganate with chlorine, any change resulting in the formation of a higher oxide of manganese or an oxide of chlorine would result. Similar experiments were tried with hydrogen chloride with the object of preparing permanganic acid.

In the first experiment the chlorine was freed from hydrogen chloride by passing through water, and was then dried by passing through two cylinders containing strong sulphuric acid. The silver permanganate was dried over sulphuric acid in a desiccator. On passing the pure and dry chlorine over this salt, no reaction took place in the cold during the space of half an hour. On heating, reaction took place with a slight explosion, and the chlorides of silver and manganese were found to have been formed. There was no appearance of the formation of a higher oxide of manganese or of an oxide of chlorine.

It was noticed in this experiment that if a trace of hydrogen chloride came into the tube with the chlorine, a rapid reaction set in. When hydrogen chloride alone (dried by sulphuric acid) was passed over the salt a violent reaction took place, even when the tube was placed in a freezing mixture. The chlorides of silver and manganese were formed, and much chlorine and water evolved. No appearance of permanganic acid was noticed.

It is proposed to study the action of other gases on the permanganates, noting the temperature of the reaction and the products formed in each case.

ON THE OCCURRENCE OF FOSSIL CARBON OF ANIMAL ORIGIN.

By G. J. Fowler.

IN the marls occurring just above the carboniferous strata at Levenshulme, near Manchester,* large numbers of nodules occur, termed by Warwickshire workmen, "fish-eyes." They form round green spots in the purple beds, with dark centres, and vary in diameter from half an inch to $1\frac{1}{2}$ inches. They are believed, from microscopical and palæontological evidence, to be coprolites. At the request of Mr. W. Brockbank, they were submitted to a chemical examination, with the result that the dark centres were found to contain carbon, which, from the above-mentioned evidence, will be of animal origin. As this source of carbon has not, so far as I am aware, been previously noted, it seemed to be of sufficient interest to chemists to warrant separate description.

The presence of carbon was established by the following tests:—

After removing carbonates by means of dilute acids, the residue was heated with potassium dichromate and strong sulphuric acid. Carbonic acid was evolved, turning lime-water turbid.

On heating with copper oxide, carbon dioxide was detected as before, and particles of reduced copper were found amongst the copper oxide.

It is difficult to decide exactly in what form the carbon occurs.

On heating, the black substance glows and disappears, evolving no odour, a fact which points to the absence of bitumen.

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* *Vide* Brockbank and de Rance, *Proc. Manc. Lit. and Phil. Soc.*, 1890-91.

On treatment with strong nitric acid, a dark brown solution is obtained, proving that the carbon is not entirely graphitic.

It does not appear to exist as a carbide of iron, as no colour is given when it is fused in a borax bead, and on heating the residue is quite white.

It is probably in the condition of non-bituminous coal. The quantity was not sufficiently large to allow of a satisfactory combustion analysis.

ON THE VITRIFIED CEMENT FROM AN ANCIENT FORT.

By G. H. Bailey, D.Sc., Ph.D.

(From the Memoirs of the Manchester Literary and Philosophical Society.)

In October, 1882, Dr. Angus Smith described before this Society a vitrified mass of stone from Glen Nevis, and gave an analysis of the stone.

In the Manchester Museum at the Owens College is also a mass composed of fragments of gneiss cemented together by vitrifaction, and said to be derived from the forts of the Picts.

Having recently visited some of these forts in the Highlands, I was interested in this specimen, and having, by the permission of Professor Boyd Dawkins, obtained a sample of the stone, I asked one of my students, Mr. W. B. Hopkins, to make an analysis of the vitrified part. The points of interest seemed to me to be :—

(*a*) Whether the materials which had been converted into the molten mass had been selected by trial in order that a body of low fusing point might be obtained or had been taken indiscriminately ;

(*b*) Whence they were derived ;

(*c*) What temperature would be required in order to bring about the fusion ?

The vitrified part showed locally a glazing, and had been distinctly fluid, but now presented somewhat the appearance of lava, being honeycombed with air spaces from which gases had apparently escaped during the fusion. Samples were taken from different parts and mixed together, and partial examination was made of the different samples with a view to detecting variations

in the composition of the mass. No considerable differences were found, except that in some parts the iron was entirely oxidised, whereas in others it still remained, for the most part, in the ferrous condition, and in addition to this there seemed to be rather more alkalies in the denser parts of the mass. The typical sample gave on analysis the following results, the sample analysed by Dr. Angus Smith being placed alongside for the sake of comparison, though I have no evidence that they are identical specimens, and indeed the analyses themselves would certainly indicate that they were not.

	Mass in Manchester Museum.		Mass from Glen Nevis.
Silica	69·59	...	68·88
Alumina.....	11·12	...	16·17
Ferric oxide	13·01	...	5·33
Lime	0·53	...	3·73
Magnesia	0·32	...	3·39
Potash	1·86	...	1·83
Soda	1·49	...	0·26
Loss on ignition ...	1·12	...	0·92

There may have been originally more alkalies present; the stone is of such a porous nature that these would be partially dissolved away by exposure to atmospheric conditions.

There is then a very low proportion of alumina, practically no lime or magnesia, and little alkali. No common mineral or rock substance, as far as I am aware, shows such a composition.

It has been suggested by previous writers on this subject that basalt was added to clay, or some such substance, to form a mass which could be fused at such temperatures as were likely to be at the command of the builders of these forts. Wood, it has been suggested, was the fuel used, and indeed in one case wood has been actually found *in situ* between the layers of stone constituting the wall.

In the case of the specimen examined, however, no basalt can have been added, for though the large proportion of iron might have lent some colour to such a suggestion, it is absolutely negatived by the absence of calcium and magnesia, which are always present in basaltic rocks.

For the same reason, and because of the low percentage of alkalies, it cannot have been a gneissose or granitic base that was

used, nor (considering the low percentage of alumina) can kaolin or clay have constituted any considerable portion of the material. In some parts of Scotland, where such forts occur, there are beds of red sandstone (of the old red sandstone age and of formations older than this), and the essential difference in composition between these lies only in a rather lower percentage of iron and of alumina and a little higher percentage of silica. These rocks, however, approach nearer to the vitrified stone than any other accessible material, and with the addition of a little iron ore, or slag, might at any rate be brought in almost exact agreement. The question of the source of the material, in this particular case, is rendered more difficult because the actual locality from which the mass was obtained is not known, and in any case it would be necessary, in order to solve such a question satisfactorily, to analyse samples of vitrified forts from different districts, and to take the results in connection with the rocks found in the district. With regard to the temperature that would be required to bring about the fusion of such a mass, I may call to notice a series of investigations which have, during recent years, been undertaken by Seger (*Thonindustrie-Zeitung*, 1886, p. 135) with a view to determine the relation of fusibility of a mixture to the proportions in which the constituent parts occur. Seger made up mixtures of silica, kaolin, and marble in different proportions, until he, by means of trials in a pottery furnace, arrived at a proximate idea of the best proportions for obtaining low fusibility. Having found this, he then made a large number of mixtures, varying the several constituents, whilst keeping others in the proportions established by the preliminary trials. It is already known that the presence of alkalies, especially soda, increases the fusibility of a mixture, and that oxide of iron acts also in the same direction. He found, however, that the keystone to fusibility rested with the relative proportion of alumina and its relation to the other bases. It is singular that in this particular the vitrified stone agrees very nearly with the proportions discovered by Seger.

If, therefore, we take this in conjunction with the peculiar composition of the vitrified stone, it would certainly seem to show that, in this case at any rate, the materials used were an artificial mixture of natural products, the proper constituents of which were arrived at by a process of trial, and that the builders of the fort

had some acquaintance with the behaviour of different substances under the action of heat, nor indeed can it be thought very remarkable if they did possess some such knowledge. It has been thought that in some cases the actual stones themselves were melted together by heat, and, however this may be, there can be no suspicion of this in the example before us. The schist, of which the fort has been built, shows no marked alteration, and certainly nothing approaching fusion. The temperature of fusion of such a mixture, as is indicated by the results of the analysis, would be about 1,200° C. to 1,300° C., and this could be readily attained by means of wood, in the manner already suggested by different writers on this subject.

A METHOD OF TESTING FOR THE PRESENCE OF SILICIC ACID.

By G. H. Bailey, D.Sc., Ph.D.

THE methods at present employed in the ordinary routine of qualitative analysis are based upon (*a*) the separation of silica on the addition of a mineral acid; (*b*) the subsequent confirmation by what is known as the skeleton bead test.

In practice, unless the solution is concentrated, no separation occurs when it is acidulated, and if the silica separates out in the iron group its identification is usually a matter of extreme difficulty. The only really satisfactory process consists in that adopted for the quantitative separation, viz., boiling down the acidulated solution to perfect dryness and extracting with dilute acid, silica being left as a residue.

This is a long and tedious operation, and unless carried out with the precautions observed in quantitative work the result is unsatisfactory.

Moreover, the confirmation by means of the skeleton bead, whilst it is serviceable in experienced hands and when operating with mineral silica, can by no means be relied upon with the silica in the forms in which it usually presents itself in the course of qualitative testing. It is with a view to supply a ready and trustworthy means of detecting silica that the following method is given.

It is known that silica, like titanic acid and several other hydrated oxides, is soluble in dilute acids when freshly precipitated in the cold, whilst if allowed to stand for some time, or if the liquid in which the hydrated oxide is suspended be heated,

it becomes much more insoluble. This property, though characteristic of several of the rare earths, is only shown amongst substances commonly occurring in quantity, by silica, and can therefore be taken advantage of in routine qualitative analysis. Moreover, it is applicable to dilute solutions from which the separation of silica by the ordinary methods in use is a matter of great difficulty.

To the cold solution, preferably diluted with water so that the precipitate formed is not too bulky, add barium chloride. A precipitate forms which redissolves on the addition of dilute hydrochloric acid. There is therefore present no sulphuric acid;* the precipitate may, however, consist of carbonate, phosphate, &c., as well as silicate.

But now, in a second tube, to some of the original solution add barium chloride as before, and, previous to the addition of hydrochloric acid, *boil* the solution for a moment. In the presence of silicic acid it will now be found that a flocculent precipitate remains after the addition of hydrochloric acid, the silica having by the boiling been transformed into the condition in which it is insoluble in dilute acids. It is well to do the experiment in both the tubes, side by side, so that the faint turbidity arising from sulphate present as impurity may be compared with the precipitate remaining in the tube in which the solution had been heated. If sulphate and silicate are present together, the barium sulphate may be filtered off after the addition of hydrochloric acid in the cold, and the filtrate, on boiling, will yield a precipitate of silica. It will be found that *after some time* the tube in which the operation was carried out in the cold also deposits silica.

* Soluble silicates usually contain a little sulphate.

THE ATMOSPHERE OF MANCHESTER.

Report drawn up by G. H. Bailey, D.Sc.

Part I.

[*This work was for the most part carried out at the Owens College, during the years* 1891 *and* 1892.]

THE great difficulty experienced in growing trees and plants in Manchester is due entirely, or almost entirely, to the existence of certain impurities in the air of this city. The Town Gardening Section of the Manchester Field Naturalists' Society decided, therefore, towards the close of 1890 to appoint a special committee, who were requested to investigate the nature and amount of these impurities, with especial reference to their origin and to their influence on animal and vegetable life. The results obtained during the last few months are here detailed.

The air impurities of a great city may be divided broadly into two classes—(1) gaseous impurities diffused throughout the atmosphere, (2) small particles of solid and liquid matter held in suspension. The gaseous impurities consist of (1) an amount of carbonic acid slightly in excess of that to be found in pure country air, (2) sulphurous acid, (3) hydrochloric acid, (4) sulphuretted hydrogen (exceptional and local), and (5) certain ill-defined organic compounds. The solid impurities (or *dust*) consist of (1) particles of carbon and carbonaceous matter from household and factory chimneys, (2) germs of microbes (of which a certain proportion are always disease germs), (3) ammonia salts resulting from the decomposition of organic matter, (4) *débris* resulting from the attrition of various living and non-living matter. It is only rarely that the air contains liquid impurities to any considerable extent—viz., when it is filled with fog. The fog consists of a vast number of globules of water held in suspen-

sion in the air; and these globules doubtless contain in an exceptionally concentrated form all soluble substances present.

It is evident that the subject of air impurity offers a wide field for investigation. The Committee has decided to give attention in the first instance to the following points: 1. The composition of the air in densely populated districts, as compared with that in thinly populated and suburban districts. 2. The relation between atmospheric impurity and prevalent sickness and mortality. 3. The extent to which smoke and noxious gases are due (*a*) to dwelling-houses, (*b*) to factories. 4. The character of the air during the prevalence of fog.

In order to obtain accurate and trustworthy information of a general nature, apparatus is being set up in the various districts of Manchester and Salford.

This report contains a record of observations made principally at the Town Hall and the Owens College.

It was decided first of all to deal with the presence of sulphurous acid in the air, for the following reasons: 1. Sulphurous acid, and the sulphuric acid to which it gives rise by oxidation, are distinctly harmful, even in small quantities, both to animals and the higher plants.* It seems probable that the effects of town fog are largely due to the excess of sulphurous acid which it contains.† 2. We know definitely that the sulphurous acid of the air arises wholly and solely from the combustion of coal, which contains from 1 to 2 per cent. of sulphur. It is a pollution especially characteristic of our great cities, and is, in our opinion, a pollution which properly directed efforts may abolish. 3. The subject is one which has scarcely been touched by previous

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* It may be noted here that, despite a long-continued tradition, gaseous sulphurous acid is not poisonous to plants of such lowly organisation as microbes. It serves, therefore, no useful purpose as a disinfectant. (*See* Miquel, *Les Microbes*, p. 298.)

† A reference to the health reports of Manchester will show how the deaths from respiratory diseases increase during the prevalence of fogs impregnated with sulphurous acid and other injurious matter. From them it will be seen that each occurrence of fog is followed by a large increase in the mortality and, *a fortiori*, in the sickness of the city. Taking the normal number of deaths per week in Manchester from such causes at 60, we find that during the period of dense fog just preceding Christmas the number rose to 200. In like manner, in London the number of deaths from diseases of the respiratory organs increased during fog from 300 to over a thousand.

observers, owing to the difficulties of estimating sulphurous acid when it is largely diluted with other gases, as in the atmosphere. We describe below a simple and accurate method which we have devised for its estimation.

Our investigations may be divided into three sections :—

(1) The determination of the sulphurous acid actually present in the air, during clear weather and during fog.

(2) The determination of the sulphurous acid (oxidised partially or wholly to sulphuric acid), in various dust deposits on leaves, &c.

(3) Observations on the variations in the clearness of the atmosphere.

Minor points of some interest have also arisen in the course of the research. Such, for instance, is the consideration of the relative amount of dust deposit on leaves in different parts of the city.

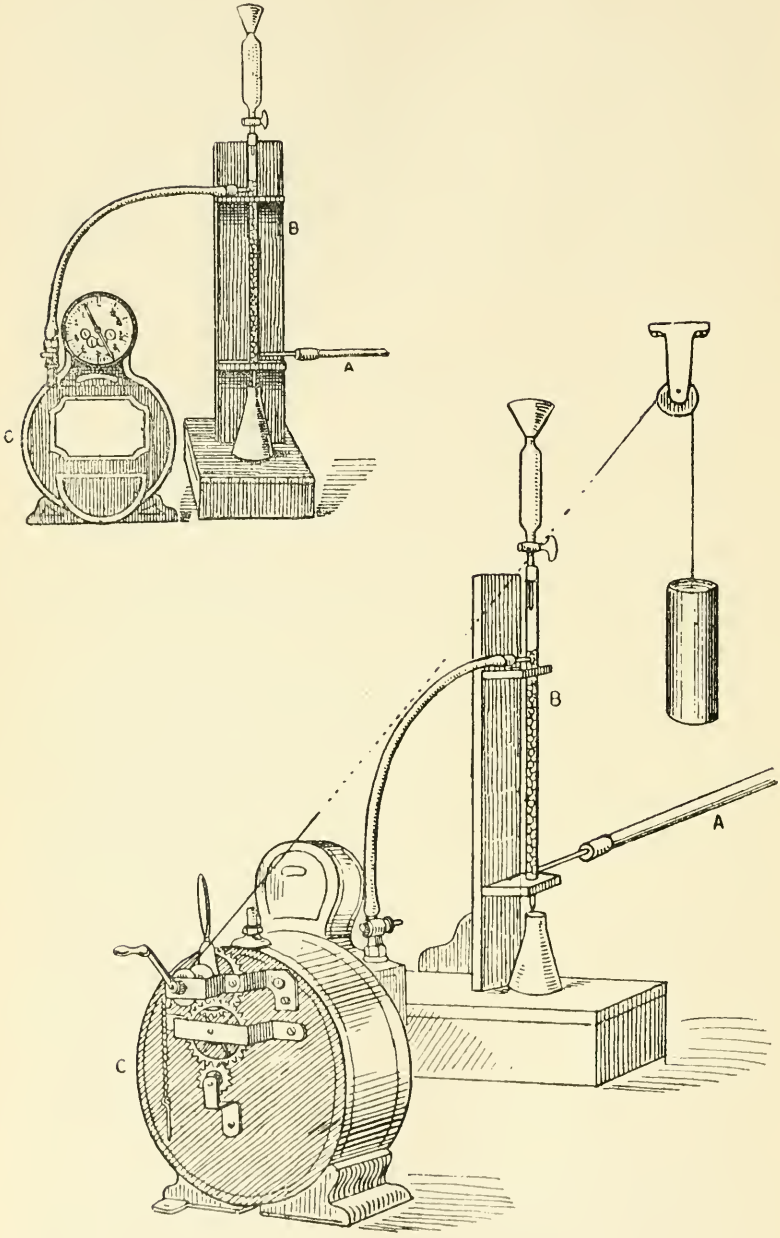
We proceed to describe in detail the experimental methods we have employed and the preliminary results we have obtained.

It is impossible, at this stage, to give a complete bibliography of the subject; but, for the convenience of those interested, we append, in a note, the names of the principal authors who have written on the subject of air impurity.*

Determination of Sulphurous Acid in the Air.

The apparatus used for the determination of sulphurous acid in the air consists of three parts—A, a long glass tube about half an inch in diameter, open at both ends, which is fixed horizontally so as to project into the open air; B, a glass tower about 30in. high and 1¼in. in diameter, open at the top, and drawn out into a fine jet at the bottom. Two side tubes are fixed to the tower, one near the bottom and the other on the opposite side near the top. The tower is filled to within one inch of the upper side piece with glass beads, and into the open top a tap funnel is inserted through a tightly fitting cork. The lower side tube is attached to the horizontal tube; the upper one, by means of wide india-rubber tubing, to a combined meter and aspirator C. This is an ordinary

* The names of these authors are as follow: Aitken, Roberts-Austen, Carnelley, Descroix, E. Frankland, P. F. Frankland, Freytag, Kny, Albert-Lévy, Miquel, Pettenkofer, Proskauer, Roscoe, Russell, Schroeder, Angus Smith, Stoeckhardt. We call especial attention to the valuable annual report issued from the Observatory at Montsouris, in Paris.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C

wet meter converted into an aspirator by attaching toothed wheels to the revolving drum, and driving the wheels by means of a wire cord passing over a pulley and carrying a weight. A series of dials registers the volume to the one-hundredth of a cubic foot. The method of conducting the experiment is as follows: About 250 c.c. of a solution of hydrogen peroxide in water, containing about one milligram of active oxygen in each cubic centimere, is poured into the tap funnel, from which it is allowed to drop on to the glass beads at the rate of about one drop a second. The liquid passes down and out at the lower end of the tube through the jet, and falls into a flask placed below. A drop of liquid which permanently fills the jet seals it effectually from the entrance of air from the interior of the room. After running through, the liquid is poured back into the funnel. The weight being wound up, the volume indicated on the dial is read off, and the drum set in motion. Once started the apparatus needs no further supervision until either the weight has reached the ground or the solution of hydrogen peroxide has run out of the funnel. The period required for this is readily determined, so that no time is lost in looking after the apparatus. A preliminary experiment made with an artificial atmosphere containing a known volume of sulphur dioxide, and a check tube with hydrogen peroxide inserted between the tower and the aspirator, gave good results, and sufficiently proved the trustworthiness of the apparatus. Determinations have been made simultaneously at the Owens College and the Manchester Town Hall. The volume of air analysed has varied from one to three cubic metres. The results are given in milligrams per cubic metre:—

1891.		Owens College.	Town Hall.
February 18.	White fog, no smell of sulphurous acid (morning)	3·14 ..	—
February 18.	White fog, slight smell of sulphurous acid (afternoon)	3·72 ..	—
February 19.	Slightly foggy at commencement only; clear rest of time (midday)	1·95 ..	—
February 19.	Clear and sunny (afternoon)	2·10 ..	—
February 19.	Moonlight and clear (evening)	1·80 ..	1·87
February 20.	Clear (midday)	— ..	1·38
February 21.	Clear (midday)	2·07 ..	—
February 24.	White fog and clear at close (midday)	3·08 ..	4·06
February 25.	Clear and sunny (10 to 5)	0·77 ..	—
February 27.	Foggy (9-30 to 12)	— ..	7·40
March 6.	Very clear, wind (9-30 to 2-30)	0·28 ..	—
March 12.	Misty, bright sun (11-45 to 1-25)	0·97 ..	—

The results show considerable variation in the amount of sulphur dioxide present in the atmosphere. The lowest result was obtained on March 6th, after two days' strong wind. The highest results were obtained on February 18th, 24th, and 27th, and on all these days there was a considerable amount of fog. The determinations made simultaneously at the Owens College and at the Town Hall show an increase in the centre of the town.

Deposits from the Air.

Deposits have been collected (1) from snow; (2) from the roofs of greenhouses; (3) from the leaves of outdoor plants in different parts of Manchester and Salford. The method employed for snow was to collect the upper layer as soon after it fell as possible from a given area. This was then melted, and the amount of sulphuric acid, and in some cases of hydrochloric acid, in the water produced was determined. By then taking the snow on each succeeding day from a fresh plot in the same locality, it could be seen how the acid and solid deposit increased, and an estimate could be formed of the amount of matter carried down each day. The following records show the amount of sulphuric acid (SO_3) and ammonia obtained, expressed in milligrams per square metre of surface:—

	Sulphuric Acid (SO_3).				Ammonia.
1890.	Wilbraham Road, Fallowfield.	York Place, Oxford Road.	Owens College.	Infirmary.	Fallowfield.
December 19, 5 p.m., fresh fallen snow	—	—	—	10	—
December 20, 11 a.m.	—	—	5·2	19	0·6
December 20, 2 p.m.	4·3	—	—	—	—
December 20, 5 p.m.	—	—	9	—	—
December 21, 11 a.m.	—	9·5	—	—	—
December 21, 2 p.m.	5·2	—	—	—	3·0
December 22, 11 a.m.	—	—	21 (258)	31	—
December 22, 2 p.m.	7·5	—	—	—	6·0
December 25, 9 p.m., fresh fallen snow	—	10 (93)	—	—	—

The amount of "blacks," where determined, is stated within the brackets. Some estimate may be formed of the actual amount when it is stated that each unit in the table represents 5·7lbs. of sulphuric acid carried down on a square mile of surface. Thus

during three days' fog there was carried down per square mile in the neighbourhood of the Infirmary (by no means the worst part of Manchester) rather more than 1½ cwt. of sulphuric acid, whilst at the Owens College the amount was over 1 cwt.; the blacks, even at the latter station, amounted to 13 cwt.; and the hydrochloric acid to about ½ cwt. Measurement has also been made of the amount of sulphuric acid carried down by rain. Through the kindness of W. T. Thiselton Dyer, Esq., F.R.S., Director of the Royal Gardens, Kew, and of Professor F. W. Oliver, of University College, London, we were able to obtain a large supply of a black deposit that had formed during the last fortnight of February on the glass roofs of the plant-houses at Kew, and on Messrs. Veitch's orchid-houses at Chelsea. Dr. Oliver also secured for us some of the cotton wool through which the air of the House of Commons is filtered. These are being examined with a view to determine the hydrocarbons, sulphuric acid, &c., which they contain. In a preliminary report we cannot give the whole of the details; and, indeed, the general results of the analysis of the Chelsea sample are characteristic of the rest.

It contained:—

Carbon	39	per cent.
Hydrocarbons	12·3	,,
Organic bases	2·0	,,
Sulphuric acid	4·33	,,
Hydrochloric acid	1·43	,,
Ammonia	1·37	,,
Metallic iron and magnetic oxide	2·63	,,
Other mineral matter, chiefly silica and ferric oxide	31·24	,,

Water not determined.

The presence of such large quantities of volatile oils explains the oleaginous character of the deposits which form from London smoke; and it has been noticed that especially in the districts of Manchester where dwelling-houses are much crowded together (*e.g.*, Hulme) the deposit has similar properties.

The leaves on which observations were made were gathered (for the most part) before much foggy weather had been experienced; there had been no rain during the previous fortnight. In the following table we have given the date at which the leaves were gathered, as well as the locality. The amount of deposit is given in milligrams per square metre of leaf surface.

1890.	Locality.	Solid deposit.	Sulphuric Acid.	Hydrochloric Acid.
December 14	Near Alexandra Park....	131	7·2	9·1
December 13	Owens College	315	10·4	17·3
December 16	Hulme	420	26·0	—
December 14	Harpurhey	443	19·0	4·4
December 14	Infirmary (hollies)	728	27·5	19·4
December 14	Infirmary (aucubas)	568	18·3	14·1
December 13	Albert Square	833	24·2	21·7
1891.				
January 17	Peel Park	374	18·0	—
January 22	Queen's Park	194	17·5	—

In nearly all cases, except where otherwise stated, the leaves examined were aucuba leaves. We see that the central districts of Manchester show by far the worst results both with regard to the amount of the incrustation on the leaves and the acid present in it. The leaves from several districts were actually acid to the taste; this was not, however, necessarily a sign of the presence of a large total amount of acid, but rather of a large percentage. Some idea will be formed of the injurious nature of such déposits on the leaves when we notice that the sulphuric acid often formed 6 to 9 per cent., and the hydrochloric 5 to 7 per cent. of the whole deposit.

Variations in the Clearness of the Atmosphere.

With the object of rendering assistance in the investigation of the composition of the Manchester atmosphere, the Medical Officer of Health has caused to be made, in connection with his department, daily examinations of certain of its optical properties.

Since the beginning of February last, Mr. Roos, senior, Statistical Clerk in the Medical Officer's Department, has made daily observations at noon, from the tower at the Town Hall, and has obtained and recorded particulars of the degrees of clearness of the atmosphere from time to time, under the constantly varying conditions of pressure and temperature of the air.

Before commencing observations, certain prominent and well-known buildings were chosen, situated in several directions—north, south, east, and west of the tower, and their distances therefrom were approximately ascertained.

The observations consisted in simply entering in a table a statement of the farthest objects which could be seen from the tower on each day, and also certain figures showing the degree of clearness with which each object could be discerned.

These observations, together with the other meteorological data ordinarily collected by the Medical Officer of Health, have been placed at the disposal of the Committee.

In concluding this preliminary sketch of the work already in hand, it is of interest to add that the Committee has been asked to undertake similar experiments in relation to the atmosphere of London, and there is also a likelihood that experiments on the same lines may be taken up in Leeds, Liverpool, and other large towns.

Sickness and Mortality in Manchester

During the Months of December (1890), *January and February* (1891).

Estimated Population, 506,325.

Week ending	Weather. (Town Hall.)	Thermometer.		Sickness (Weekly Numbers).		Deaths (Weekly Numbers).	
		Maximum.	Minimum.	General, treated at Public Expense.	Infectious, reported to Medical Officer.	All causes.	Respiratory Diseases and Phthisis.
Dec. 6	Dry and cold, thawing	48·6	29·8	780	70	244	85
„ 13	Dry East winds, hard frost, some fog ..	40·1	25·8	719	83	238	87
„ 20	Ditto ditto	40·1	18·6	672	70	294	121
„ 27	Ditto ditto (dense fog three days)	40·8	15·8	448	56	393	204
Jan. 3	Overcast, severe frost	41·8	26·0	691	59	328	165
„ 10	Overcast (foggy two days)	40·8	21·7	801	52	341	153
„ 17	Ditto ditto	43·8	27·8	853	66	336	156
„ 24	Overcast	48·7	17·0	708	51	278	109
„ 31	Overcast (clear two days)	51·6	36·0	818	61	263	95
Feb. 7	Ditto ditto	51·4	34·7	802	52	211	78
„ 14	Overcast	50·1	37·2	866	62	232	91
„ 21	Dull (dense fog two days)	52·7	27·6	787	54	291	104
„ 28	Clear (dense fog one day)	56·7	29·0	929	62	257	113

Part II.

Sulphurous Acid and Organic Matter in Air.

The weight of air inspired by a human being in the course of a day is very much greater than the whole of the solid and liquid food taken. And, moreover, modern research has shown that disease is propagated and serious injury done to the system by means of organic and other impurities of which air is the vehicle.

Yet, although methods have been worked out for the analysis of foodstuffs and water, and the most elaborate arrangements have been made to insure that these materials shall be supplied in a state of sufficient purity, no adequate steps have been taken with regard to air. It is true that a large amount of information has been collected with regard to the distribution of carbonic acid in the air, and this has led to improvement in the sanitary condition of dwellings in so far as it has been the means of promoting improved ventilation. But even for such a purpose the knowledge we have gained is insufficient, since the other and far more hurtful impurities of air have been almost wholly disregarded. Furthermore, the problem of the air outside the dwelling, a problem which is especially pressing in large towns, has been very much neglected. Indeed, with the exception of Dr. Russell's most interesting reports on the impurities of London air, hardly anything has been published in recent years relating to the sulphurous acid and organic matter in town air.

In the neighbourhood of glass works, or where copper smelting or similar industries are carried on, large quantities of sulphurous acid are thrown into the air, and in a district like South Lancashire there is no doubt a considerable contribution from the manufacture of sulphuric acid and alkali. As our inquiry deals

especially with town air, the pollution we have to consider arises for the most part from the combustion of coal in the domestic firegrate and for raising steam; and, indeed, in any case, the reports of the Alkali Inspector show that the amount of sulphurous acid given out by the alkali works in South Lancashire is quite trivial compared with that produced by the combustion of coal. Analysis of the air in large towns should afford a measure of the extent of pollution by the burning of coal as at present carried on. It is also in the large towns that we may expect to find evidence of excessive quantities of organic matter in the air, and this more especially in regard to the foul condition of water-courses and to the tendency that nowadays prevails to make the atmosphere the receptacle for the effluvia of sewers and refuse heaps, &c. At times when the proper diffusion into the higher regions of the atmosphere is interfered with, or when there is very little horizontal movement of the air, the accumulation of such impurities takes place to an alarming extent. A determination of the impurities of air to be of value in populous districts should, therefore, not be confined merely to the measurement of the carbonic acid, but include especially—

(*a*) The amount of sulphurous (and sulphuric) acid.

(*b*) The amount and (so far as possible) the nature of the organic matter.

(*c*) The number and the character of the micro-organisms.

The Air Analysis Committee of the Manchester Field Naturalists have been engaged during the past eighteen months in carrying out investigations in various directions with a view to ascertain the pollution in different districts. Without the hearty co-operation of a number of observers who undertook the superintendence of the apparatus it would not have been possible to carry on the work, and the Committee desire especially to record their indebtedness to Alderman W. H. Bailey (Salford), J. Taylor, Esq. (Blackfriars), T. Guest, Esq. (Ancoats), James Hart, Esq. (Hulme), A. Paulsen, Esq. (Town Hall), for their valuable assistance.

In the following tables are given the maximum, minimum, and average observations of sulphurous acid during the year just ended August, 1892.

MAXIMUM AND MINIMUM AMOUNTS OF SULPHUR RECORDED FOR EACH MONTH, IN THE AIR OF MANCHESTER AND SALFORD,

Expressed in milligrams of SO_3 per 100 cub. ft. of air.

	Owens College.		Hulme.		Town Hall.		Ordsall.	
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.
Sept. 1891	3·4	0·7	2·4	1·6	2·7	1·0	—	—
Oct. ,,	4·7	0·5	4·4	2·4	6·8	1·2	—	—
Nov. ,,	9·8	2·1	8·7	1·7	14·0	2·9	10·5	2·7
Dec. ,,	22·6	2·3	21·1	2·4	20·5	3·4	32·2	2·7
Jan. 1892	12·1	3·3	11·9	4·0	12·7	4·7	17·7	5·7
Feb. ,,	11·6	4·2	12·0	3·4	8·9	5·6	13·4	4·7
Mar. ,,	8·5	3·9	11·0	6·6	26·7	7·6	21·2	4·0
April ,,	12·7	4·1	18·0	6·6	18·5	5·1	20·5	5·8
May ,,	5·1	2·7	5·3	2·7	4·1	2·7	6·4	5·1
June ,,	4·7	2·1	5·5	3·2	4·4	1·3	5·6	2·7
July ,,	3·7	2·0	8·3	3·4	2·4	1·0	5·5	4·0
Aug. ,,	2·9	2·4	6·8	3·6	4·4	3·0	5·1	3·4
Means	8·5	2·5	9·6	3·5	10·5	3·3	12·5 ?	3·5 ?

The results for Blackfriars Street (Salford) are not given, partly because the returns are not quite complete, but also since they essentially agree with those for the Town Hall. The returns for the Ancoats Station are also unfortunately too incomplete to be included in this table.

Average Amount of Sulphur,

Expressed as SO_3 per 100 cub. ft. of air, for each Month, as obtained by taking a mean of all the determinations made.

	Owens College.		Hulme.		Town Hall.		Ordsall.	
	No. of determinations.	Average Result.	No. of determinations.	Average Result.	No. of determinations.	Average Result.	No. of determinations.	Average Result.
Sept. 1891	8	1·5	4	1·8	3	2·0	—	—
Oct. ,,	15	1·7	4	3·1	6	3·4	—	—
Nov. ,,	17	4·3	15	3·7	13	6·2	11	5·9
Dec. ,,	14	9·3	16	9·5	7	10·1	20	9·5
Jan. 1892	12	6·3	9	7·3	5	9·1	7	10·9
Feb. ,,	16	5·9	12	7·5	4	7·1	12	7·4
Mar. ,,	16	6·5	11	8·9	6	12·7	14	9·8
April ,,	16	6·0	10	9·7	4	10·3	13	12·6
May ,,	5	4·1	4	3·8	4	3·4	5	5·6
June ,,	8	3·2	5	4·2	4	2·6	4	4·5
July ,,	5	3·2	4	5·7	3	1·7	3	4·9
Aug. ,,	5	2·7	4	4·8	5	3·9	5	4·3
Mean for the six months Nov. to Ap'l		6·4		7·8		9·25		9·4
Mean for the rest of the year		2·7		3·9		2·8		4·2?

So far as the records go for the district of Ancoats, the numbers are very similar to those for the Ordsall district of Salford, sometimes a little better, sometimes worse.

Organic Matter.—The method of determination was as follows: 200 cub. ft. of air (500 cub. ft. may be needed in clear weather, and 100 cub. ft. be quite sufficient in time of fog) are aspirated through a tube packed not too tightly with a column of 6 or 8 inches of glass wool. The organic matter and a small portion of the sulphurous acid is retained. The glass wool is now thrown into an acid solution of permanganate of potash of known strength. By withdrawing almost immediately with a pipette a fractional portion of the solution and titrating, it will be found that some reduction of the permanganate has taken place, and the oxygen equivalent of this can be measured. Similarly, portions of the permanganate are withdrawn at the end of one hour, six hours, and twenty hours, and the amount of reduction estimated.

After this follows digestion for an hour at 50° C. to ascertain any further reduction, and finally a known quantity is distilled with excess of alkali to determine the ammonia and hence the nitrogen present in the organic matter. From these data we gain some insight into the quantity of organic matter present, except such as remains unoxidised at 50° C. and may be neglected, and also into the nature of it.

Omitting the deoxidation which takes place almost immediately, which we may take as being due to sulphurous acid, we should find, for instance, an ordinary dusty and smoky atmosphere give low records for the one and six hour periods, whilst an atmosphere charged with *noxious* organic matter, such as usually occurs in time of fog, will give high records for the one and six hour periods proportionally to the readiness with which the organic matter decomposes.

The numbers on the following page were obtained in actual experiments carried out during the past autumn and winter months.

Suspended Organic Matter in the Air,

Given according to the number of milligrams of Oxygen required to oxidise the Organic Matter in 1,000 cub. ft. of air.

Date.	Locality.	Organic Matter.				Direction of Wind.	Remarks on Weather.
		A	B	C	Total.		
1891.							
Sep. 16	Owens Coll.	0·7	nil	nil	0·7	W	Dull day.
„ 16	Hulme	1·1	„	„	1·1	„	„
„ 16	Blackfriars	2·4	„	„	2·4	„	„
Oct. 20	Owens Coll.	0·8	0·4	1·3	2·5	S.S.E.	Gleamy. Air clear
„ 22	„	3·0	3·2	0·8	7·0	E.S.E.	„ Rather hazy.
„ 24	„	7·3	5·2	1·0	13·5	S.E.	Light fog.
Nov. 6	„	6·0	6·5	1·7	14·2	W.N.W.	„
Dec. 21	„	14·6	5·2	8·2	28 0	Calm.	Dense fog.
„ 22	„	7·5	16·9	5·3	29·7	„	„
„ 22	Ancoats	19·3	4·5	5 7	29·5	„	„
„ 23	Owens Coll.	17·1	14·3	9·3	40·7	„	„
1892.							
July 30	„	3·0	2·8	1·3	7·1	N.N.E.	Gleamy.
Sep. 6, 7, 8	„	2·5	1·5	0·4	4·4	Southerly	Dull, with occasional sun. Air hazy.

The foregoing are quotations from a considerable number of determinations which have been made. The experiments were so carried out as to show whether the organic matter was of a readily decomposable (and hence putrescible and noxious) kind, or consisted of comparatively uninjurious particles of dust and soot.

Thus, column A may be taken to represent very readily putrescible matter; column B, less readily putrescible matter; column C, soot and dust.

On October 20th, about 30 per cent. of the organic matter was of a noxious character, and more than 50 per cent. was of such a nature that it failed to be oxidised in 20 hours at the ordinary temperature, and only became acted upon at 50° C. That is, at least 50 per cent. of the organic particles in the air consisted of some such substance as coal dust and smoke. On October 24, on the other hand, over 50 per cent. was organic matter of the more noxious kind, whilst the difficultly oxidisable and less injurious organic particles constitute less than 10 per cent. of the whole. Following in the same way the other lines of figures, we are able to make similar deductions.

Moreover, comparing together the numbers obtained in experiments carried out simultaneously in different localities, it is possible to say which locality shows the greater amount of noxious pollution. The district of Ancoats is more densely populated and nearer the centre of the city than that in which the Owens College is situated. We note that on December 22 the total amount of oxidisable organic matter in the air of these two localities was practically the same, but the *nature* of the organic matter was widely different, for whilst in the Owens College district less than 25 per cent. was of the more noxious character, the percentage in the Ancoats district was 65.

Occurrence of Fog.

By means of a staff of observers in different parts of the city and suburbs, a large amount of information has been collected regarding the nature and distribution of fog.

The points to which attention has been particularly directed are: (*a*) The time during which the fog lasted; (*b*) whether generally distributed or confined to certain localities; (*c*) its nature, especially as regards density and odour. There was, on the whole,

much less fog last winter (1891-2) than during the previous one, and hardly any serious and prolonged occurrence of fog.

This is largely owing to the fact that the barometer was during the whole period remarkably variable. The anti-cyclonic periods, during which the air is still, were indeed only four in number—the beginning and end of November, the middle of December, and the beginning of April, and each of these was accompanied by fog extending more or less over several days. The following are the dates when fogs prevailed:—

Dense Fog Lasting All Day or Nearly So.

October .....24.
November ... 6, 7,* 23,* 27.
December ...21, 23, 24, 25.
January ..... 4, 9, 12, 15, 19, 20.
April ..... 1, 2, 5, 6, 11.

Fog Confined to Morning or Evening Hours.

October .....25, 29, 30, 31.
November ... 3, 4,* 5,* 14,* 21, 22,* 24, 26, 29, 30.
December ... 2, 7,* 11,* 14,* 17, 20, 22, 30.*
January ..... 7,* 8,* 10,* 11,* 14,* 17, 18, 22,* 23,* 25,* 26.
February ... 6,* 8,* 10,* 11,* 12,* 13,* 16,* 18,* 20,* 22, 24.
March.....13, 18, 21,* 23, 24,* 29, 30, 31.
April ..... 3, 4,* 12,* 19.*

When the fog was confined to some particular part of the city, the date is marked with an asterisk. On 20 occasions, therefore (two of these partial), dense fog has been recorded, and on 56 occasions (30 of these partial) the fog has been confined to the morning (usually 8 to 11 o'clock) or evening (usually 6 to 9). It may be added that the whole of the October fogs were shallow, hardly extending above the houses, so that the blue sky could be seen directly overhead, even through the fog.

Summarising a mass of details which have been collected, we draw the following conclusions with regard to the fogs of the past winter:—

(1) The fogs almost invariably accompany a steady or steadily rising barometer, especially if there is also a fall of temperature.

(2) They were, when partial, most likely to occur in the vicinity of streams of water; for instance, there was frequently dense fog

over the Irwell near Broughton, and over the Medlock near All Saints, when the rest of the city was almost clear.

(3) They were most suffocating and noxious in the neighbourhood of the Irwell between Cornbrook and Blackfriars.

(4) The most central part of the city of Manchester, the triangular area having the Exchange Station, the Central Station, and London Road Station at its corners, was usually more free from fog than the surrounding area. This was particularly the case with the fogs which were of short duration.

(5) The London fogs, so far as the more central parts of the City are concerned, were more noxious and contained more sulphurous acid than the corresponding Manchester fogs, though the difference is not very considerable. Liverpool seems to have fewer fogs, a clearer air, and really bad fogs seldom occur—doubtless owing to its sea breeze.

In concluding the remarks on this subject, it may be pointed out that the nature of the air at different heights during the prevalence of fog has not yet been investigated; an early opportunity will be taken of carrying out experiments in this direction.

Observations on Rain and Snow.

It was evident to us from the first, that information obtained from samples of rain taken by exposing the collecting vessel for a prolonged period is of little value. Evaporation and the constant accumulation of "blacks," carrying their quota of sulphuric acid, ammonia, &c., are in themselves sufficient to completely vitiate the results of such experiments.

In each case, therefore, except where otherwise stated, it may be assumed that the samples analysed consisted of freshly-fallen rain. Furthermore, for the concentration of the rain before the analysis, a gas flame must not on any account be used, or the sulphuric acid will be much too high. We have employed a spirit lamp. Samples of snow were, however, taken in some cases on successive days, as it was possible in this way to arrive at a fair approximation to the amount of "blacks" and other impurities that are actually carried down each day.

We ought to add that the degree of impurity of the rain is conditioned also by the nature of the fall; large drops and heavy rainfall will, *cæteris paribus*, give a much purer rain water than a fine drizzle.

Analysis of Samples of Rain and Snow Collected.

Date.	Locality.	Blacks.	Chlorine.	Sulphuric Acid.	Direction of Wind.	Remarks on Weather.
		In grains per sq. yard.	In parts per million.	In parts of SO_3 per million.		
1891.						
Nov. 11	York Place	—	5·7	11·3	E.S.E.	Dull and squally.
,, 11	Manchester Grammar School	—	21·0	42·3	,,	,, ,,
,, 11	Kersal	—	—	26·1	,,	,, ,,
Dec. 12	York Place	—	—	70·6	S.	Dull. Fine drizzle.
1892.						
Jan. 7	Owens College	1·0	3·3	11·7	N.W.	Snow. Air moderately clear.
,, 7	Kersal	0·7	—	2·6	,,	,, ,,
,, 8	Owens College	2·7	6·0	17·8	S.W.	,, ,,
,, 11	Piccadilly	21·5	11·2	15·0	N.	Bright and sunny, but had been foggy on 2 previous days.
,, 11	York Place	9·2	12·1	9·5	,,	,, ,,
,, 11	Owens College	12·3	5·7	6·2	,,	,, ,,
,, 12	,,	—	37·2	37·3	S.S.E.	Drizzle. Air hazy.
,, 18	,,	—	8·0	25·3	E.	Dull day.
,, 19	,,	—	22·1	39·6	E.N.E.	Fine rain from dark smoke cloud.
March 10	,,	16·7	18·4	28·2	W.N.W.	Gleamy, with snow showers.
,, 10	York Place	10·7	9·1	19·6	,,	,, ,,
,, 14	Owens College	19·3	13·7	19·3	E.S.E.	Cloudy. Snow.
,, 14	Piccadilly	26·0	22·4	37·0	,,	,, ,,
May 13	York Place	—	3·9	7·5	S.	Air calm. Heavy rain.
,, 13	Owens College	—	3·7	8·2	,,	,, ,,
,, 16	,,	—	12·9	12·6	W.N.W.	Strong breeze.
July 19	,,	—	2·0	6·8	S.	Heavy and continuous rainfall.
Aug. 19	York Place	—	1·5	6·9	E.	Heavy rain.

It will be seen that when the air of the town is clearest, the rain contained about 6 parts per million of sulphuric acid, whilst during less favourable periods over 40 parts were recorded.

Nor were the conditions under which these samples were obtained such as to indicate that these are extreme records, at

times results much exceeding 40 parts are to be expected, and 6 parts cannot be regarded as a minimum record.

The chlorine varies in the most extraordinary manner; how far it arises from sewage contamination of the air, how far from salt works, or muriatic acid works, or is salt carried from the sea, it is impossible to say, and probably all these agencies contribute their quota in constantly varying degrees.

Apropos of analysis of rain, we may quote the results of the examination of *rime*, which collected on aucuba leaves in York Place between December 21st and December 25th, and which showed 89 parts of sulphuric acid per million! whilst that collected on a glass plate at the same place between December 19th and December 25th gave 386 parts of sulphuric acid per million, and 9·2 grains of blacks per square yard.

Observations on Light in Manchester and Suburbs.

Previous to 1870 a large number of observations were made by Roscoe and Thorpe for the purpose of ascertaining the intensity of sunlight at different seasons, and in different localities.

It was found that the intensity of clear sunlight recorded by a photometric method on a horizontal surface is directly as the altitude of the sun; that the intensity in the tropics is considerably greater than that under similar circumstances at Heidelberg, and still greater than that measured in this country; and, finally, that a very large proportion of the light was cut off when the atmosphere was at all hazy. Recently Brennand has published a series of measurements, made partly at Dacca and partly in Somerset, which show a general agreement with the results of Roscoe and Thorpe; and by means of ingenious appliances he has been able to record the intensity of light received from different parts of the sky.

In addition to these important investigations, we have also the ten years' sunshine records made under the auspices of the Meteorological Society. Valuable as these investigations are, they are mainly devoted to the consideration of sunshine.

Hitherto, no sufficient attempt has been made to ascertain how the light received within a town area compares with that of the suburbs, or of country districts removed from towns. It is found, as a matter of fact, that the conditions of town air are

most unfavourable to plant life, and, for the matter of that, to human beings; but very little definite information is to hand indicating what these conditions are. The Air Analysis Committee of the Manchester Field Naturalists have been engaged during the past year or so in investigations on the impurities of town air, and have supplemented their work by observations on the extent to which the light rays are cut off by haze and smoke.

Although sunshine records are taken at the Meteorological Station in Manchester, it has been our object to measure not the sunshine only (sometimes for weeks together we have none), but the total light received each day. These measurements were made at some fifteen stations at different parts of the city and suburbs.

The apparatus used in the researches already described was much too elaborate for us, and as others may also be interested in making such comparative records in their own district, we describe the method adopted. After an examination of various media, we were led to adopt with some modification a process suggested by Leeds, and used to some extent by Angus Smith. If a solution of potassium iodide be mixed with dilute sulphuric acid and exposed to light, iodine is liberated. The reaction which takes place may be represented by the following reactions:—

$$KI + H_2SO_4 = KHSO_4 + HI.$$

and

$$2HI + O = H_2O + 2I.$$

If the solutions be too concentrated the action goes on in the dark, and if too dilute the amount of iodine liberated on a dull day is hardly measurable with any degree of accuracy. Fortunately there exists a mean between these two limits. The solution of potassium iodide contains 20 grams to the litre, and the sulphuric acid 11·85 grams (H_2SO_4) to the litre—*i.e.*, by mixing equal volumes of the solutions, the potassium iodide and sulphuric acid are present in the proportions required by the equation given above. The solutions are kept separate, and mixed just before being exposed, 10 c.c. of each being used. The mixture is placed in a two-ounce stoppered bottle (the 45 c.c. of air space remaining above is amply sufficient to supply the oxygen necessary for the reaction to proceed) and placed on a white plate in a situation open, as far as possible, on all sides. By putting the bottle out after dark and taking it in after dark on the following

evening, we have the cumulative amount of iodine liberated during the day, and so on from day to day. The iodine liberated is measured by noting the amount of a sodium thiosulphate solution of known strength requisite to just decolourise it; we have thus a comparative measure of the light received during the time of exposure.

Similar solutions have been exposed under as nearly as possible the same conditions at a large number of stations, and the record of the light for each day has been taken during the past twelve months. The Air Analysis Committee desires to express its indebtedness to the large staff of experienced observers who have taken the observations. The stations were:—

Didsbury	The Park	Mr. W. Holt.
Fallowfield	Wilbraham Road	Miss Cohen.
Rusholme	Birch Hall	Professor Dixon.
Oxford Road	York Place	Dr. Bailey.
Longsight	Birch Lane	Mr. W. E. Sims.
Ardwick	The Polygon	Mr. T. C. Lamb.
London Road	Mayfield	Mr. T. H. Sims.
Hulme	Embden Street	Mr. J. Hart.
Greenheys	Gore Street	Mr. A. McDougall.
Miles Platting	Vickers Street	Mr. W. Irwin.
Oldham Road	Meteorological Station	Mr. Hazzelwood.
Kersal	Vine Street	Dr. Schunck.
Cheetham	Temple House	Dr. Dyson.

The character of the weather was recorded at York Place, whilst the direction of the wind and the hours of sunshine, where given, are from the Report of the Medical Officer of Health, as taken at the Oldham Road Meteorological Station.

The results are in all cases expressed in milligrams of iodine liberated per 100 c.c. of liquid exposed.

It may be added that we have actually ascertained by experiment that the amount of iodine liberated is proportional to the light received; the solution is nevertheless more affected by the more refrangible rays of the spectrum than by the less refrangible.

The rays affecting the solution are almost completely absorbed by a solution of bichromate of potash, and also by an alcoholic solution of chlorophyll.

In the experiments which we have taken up our main objects were: (*a*) To obtain a comparative measure of the total amount of light at various parts of a city and suburban area; (*b*) to ascertain the relation between the amounts of light received during different seasons of the year.

We desired, further, to make the observations on such a scale that it would be possible to determine how far fog, smoke, and atmospheric conditions in general, as prevailing in towns, affect the results.

Let us first determine how the light received at any station is affected by the direction of the prevailing wind at the time, which may either come to the station over the town or from the country. Specially adapted for this purpose are the observations taken at the Hulme station, which lies rather less than half a mile from the S.W. border of the city, and the Oldham Road and Miles Platting stations, which lie about the same distance from the N.E. border.

Let us now take the average of the results of a number of days when the wind was from the N. or N.E. points, and also those when the wind was from the S. and S.W. points, and compare for these special directions of the wind the two stations on the N. or N.E. quarter of the city with that on the S. or S.W. quarter. As a mean of twenty days selected at random—

		Wind in S. or S.W.	Wind in N. or N.E.			Average Record.
Hulme	gives	65	39	per cent. of	Didsbury	49
Oldham Road	,,	39	86	,,	,,	55
Miles Platting	,,	47	93	,,	,,	67

With the wind blowing from the suburbs the record at Miles Platting is nearly as high as at Didsbury, double of what it is when the wind blows from the city. The same thing holds in a rather less pronounced manner for Hulme. We can therefore have no doubt that it is really the smoke which cuts off our light, and this in a very marked degree. The following table shows the average record *per day* for each station during the year September, 1891, to August, 1892.

The results for week days and for Sundays have been collected and given separately.

Locality.	1891.				1892.								
	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apl.	May.	June.	July.	Aug.	
Didsbury	39·6	24·7	10·4	9·5	7·2	15·4	25·9	38·7	51·0	55·3	44·2	36·8	Week days.
	32·0	30·0	11·0	11·0	15·6	11·1	22·6	55·0	52·6	60·5	32·6	39·0	Sundays.
Birch	—	22·3	10·6	6·7	6·6	13·3			40·1	38·5			Week days.
		26·7	11·2	11·7	9·1		—	—	53·4	42·0	—	—	Sundays.
Longsight	—	20·4	8·6	6·9	3·9	14·4	19·8	25·9	40·2	27·5			Week days.
		23·4	9·9	10·0	7·2	9·2	15·4	44·2	45·4	31·2	—	—	Sundays.
Whitworth Park	32·7	17·6	5·5	3·6	2·6	11·7	21·0					30·1	Week days.
	27·0	22·6	7·5	5·9	5·3	8·1	20·0	—	—	—	—	32·0	Sundays.
Greenheys	—	—	—	5·7	—	13·9	17·3	16·5	28·9	20·4			Week days.
				7·0		7·8	15·5	25·8	27·6	22·0	—	—	Sundays.
Hulme	21·0	15·2	5·1	4·7			11·0	14·7	27·5	22·0	23·6		Week days.
	21·2	20·8	4·4	5·1	—	—	9·0	22·0	21·2	22·0	18·4	—	Sundays.
London Road	—	15·2	6·6	3·9	4·3	12·7	15·9	27·8	30·6	30·5	28·2	24·1	Week days.
		19·5	6·8	6·1	9·0	9·0	18·1	43·0	37·6	41·0	25·2	28·5	Sundays.
Oldham Road	25·4	12·8	4·7	3·2	2·3	12·1	13·6	24·3	32·7	25·5	26·3	21·3	Week days.
	19·8	17·6	6·0	3·4	4·7	10·0	20·8	38·5	34·8	36·0	20·6	23·2	Sundays.
Miles Platting	—	—	5·8	4·0	4·7	14·6	19·0	28·0	34·1	30·3			Week days.
			6·4	5·5	7·1	9·7	24·0	45·7	36·8	40·0	—	—	Sundays.
Hours of Sunshine at Oldham Rd.	3·41	2·0	0·26	0·13	0·45	1·80	3·03	4·4	5·35	5·24	4·63	3·55	Week days.
	3·35	2·9	0·16	0·62	0·76	0·28	2·80	8·7	5·00	6·40	3·70	3·90	Sundays.
Average hours per day between sunrise and sunset (approx.)	12·3	10·8	9·0	7·8	8·3	9·8	11·9	13·9	15·3	16·4	16·0	14·4	

The question of the clearness of the air on Sundays as compared with the other days is one of interest as affording some indication of the effect of stoppage of works on Sundays, though we cannot draw any conclusions from a *direct* comparison of these numbers, because it may so have happened that the Sundays have been finer or duller days than the week days, as the case may be. If, however, we take Didsbury, the station least affected by smoke, situated as it is five miles from the centre of the city, the numbers there will indicate more nearly how far the variations are dependent on the weather. For instance, in September, 1891, the average record for week days was 39·6, for Sundays 32·0, showing that the week days were on the average brighter in this month; but if we take January, 1892, the respective values are 7·2 and 15·6, showing that the Sundays of January were much brighter than the week days. If now we reduce the week-day values for Didsbury and the Sunday values each to 100, and calculate all the other numbers in the same proportion—*i.e.*, if we find the percentage which each station bears to Didsbury for week days and for Sundays, we shall have a means of ascertaining how far the town stations are affected by smoke and conditions other than the meteorological. When this has been done it is found that the percentages which the several stations bear to Didsbury as an average of the whole year are :—

Birch	on week days	84	per cent.	of Didsbury	record.
,,	,, Sundays	89	,,	,,	,,
Longsight	,, week days	73	,,	,,	,,
,,	,, Sundays	75	,,	,,	,,
Whitworth Park	,, week days	65	,,	,,	,,
,, ,,	,, Sundays	70	,,	,,	,,
Greenheys	,, week days	59	,,	,,	,,
,,	,, Sundays	57	,,	,,	,,
Hulme	,, week days	49	,,	,,	,,
,,	,, Sundays	49	,,	,,	,,
London Road	,, week days	62	,,	,,	,,
,, ,,	,, Sundays	70	,,	,,	,,
Oldham Road	,, week days	54	,,	,,	,,
,, ,,	,, Sundays	61	,,	,,	,,
Miles Platting	,, week days	66	,,	,,	,,
,, ,,	,, Sundays	71	,,	,,	,,

Comparing these numbers, we see that the atmosphere was for the period described no clearer on Sundays than week days in the districts of Hulme and Greenheys, and very little clearer in Longsight. That in Birch, Whitworth Park, and Miles Platting (also Kersal) districts the record on Sundays is about 7 per cent. higher than on week days; whilst in the distinctly urban districts of London Road and Oldham Road the Sunday record has an advantage of about 13 per cent. over the week day.

The stoppage of works, the closing of places of business, and the general movement of the population towards the outskirts on Sunday therefore clears the atmosphere of the city, but not to such an extent as to warrant the assumption that the works contribute the lion's share of the smoke.

Perhaps still more striking and instructive is the fact that London Road comes out in the results more favourably than Hulme. We must, however, bear in mind that quite in the heart of the city there is a space about a square mile in extent, a triangle having the railway stations at its corners, in which there are hardly any dwelling-houses, and, moreover, the warehouses and shops which for the most part cover that space are lofty, and consequently the flues from the fires are long, and allow more perfect condensation of smoke. In Hulme, however, we have hardly any works, the dwelling-houses are mostly low, and built very close together. The comparison is an interesting one, affording as it does distinct evidence that the domestic house is a very large contributor to the smoke which hangs over our towns, but that as the population migrates outwards and the more valuable land in the centre of the city is taken up by warehouses, &c., it may quite well happen that the condition of the city area may become quite tolerable. As further evidence tending in the same direction, it may be mentioned that the city area defined above has been in many cases during the past winter, quite free from fog when districts nearer the borders of the city have been enveloped in it, this being especially the case with the short-lived morning or evening fogs.

The conclusions which may be fairly deduced from these results are:—

(1) That November, December, and January were by far the darkest months, especially within the city.

(2) That the average record in densely populated districts is during the winter months about one-half that of the suburbs, and it may be added less than one-tenth that of a moderately bright April day.

(3) That the active effect of sunshine (numbers stated in a previous report) for the suburbs of large towns, *e.g.*, Didsbury and Kew, is in the winter months one-third of that obtained at Torquay.

(4) That the smoke and haze almost always associated with a town atmosphere, even during the brightest weather, are extremely potent in cutting off the chemically active portion of the light rays.

(5) That in both 1891 and 1892 the atmosphere has been found much the clearest in the month of September, a result which receives further corroboration from the fact that during that month the amount of organic particles and sulphuric acid found has been lower than in any other month. Further experiments will show whether this is generally the case.

(6) That the town atmosphere compares most unfavourably with that of the country, especially in respect of clearness during prolonged periods of high and steady barometer, when there is very little horizontal movement of the air to carry off the impurities.

ON THE REACTION OF HYDROGEN WITH CHLORINE AND OXYGEN:

A STUDY IN CHEMICAL EQUILIBRIUM.

By J. A. Harker (*Dalton Chemical Scholar in the Owens College, Manchester*).

(*Translated from the Zeit. Phys. Chem.*)

At the beginning of the present century, Claude Louis Berthollet* enunciated his well-known law relating to the action of mass in chemical systems. His work, however, seemed almost to have been forgotten till some fifty years later, when, almost simultaneously, Debus† and Bunsen‡ published papers, the former dealing with the case of liquids, while the latter treated of gases.

Since in most cases gases exhibit much simpler relationships than liquids, it might have been expected that a generally applicable theory for the chemical action of mass should have been found for the former rather than the latter. But the opposite has been the case. The theory enunciated in 1867, by Guldberg and Waage, for reversible reactions, soon found application to mixtures of liquids and to solutions, while the attempt to apply it to gases was met by several difficulties which remained for some time insuperable. Bunsen investigated the action of mass when oxygen was exploded with mixtures of hydrogen and carbonic oxide in varying proportions. His results were anomalous. We now know that this was due to the fact that one of the gases used

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* C. L. Berthollet.

† H. Debus, *Ueber chem. Verwandtschaft Ann. Chem. Pharm*, 1853, vol. lxxxv, 103.

‡ R. W. W. Bunsen, *Untersuchungen über die Chemische, Verwandtschaft Ann Chem Pharm*, 1853, vol. lxxxv, 137.

in these early experiments, viz., carbon monoxide, exhibits a quite unexpected behaviour toward oxygen, and that one of the products of the change, steam, was removed by condensation during the reaction—discoveries made by H. B. Dixon.

The theory of Guldberg and Waage may be enunciated as follows: If two bodies, A and B^1, react with one another, giving A^1 and B, and if this reaction is reversible so that the two opposite changes

$$A+B^1=A^1+B \quad \text{and} \quad A^1+B=A+B^1$$

take place at the same time, then the number of molecules of each of the bodies remaining at the end of the reaction, when equilibrium has been reached, viz.,

$$pA+p^1A^1+qB+q^1B^1,$$

will be given by the equation

$$\frac{p}{p^1}=k^2\frac{q}{q^1}$$

where k^2 denotes a constant quantity called the "co-efficient of affinity" for the particular system of bodies.

This is not absolutely constant, but changes with temperature, pressure, and other external conditions. The limits between which it remains constant for fluids are, however, generally tolerably wide, while for gaseous systems almost every observation gave a new value of the constant.

A. Horstmann* found the reason of this irregularity in the water vapour present in the gases used, and showed that the same values for the co-efficient of affinity were obtained in different experiments if the gases were dried, and the same quantity of oxygen was added to a definite volume of the two combustible gases, mixed in any ratio to one another.

H. B. Dixon,† in a research which he began about the same time, and without having heard of Horstmann's results, showed that well-dried carbonic oxide burns with oxygen only with great difficulty, and that consequently the process so often studied is not, as was believed, a mere contest between the two combustible gases, carbonic oxide and hydrogen, for the oxygen present, but that the latter goes at first entirely to the hydrogen, and only

* *Verhandlung des Naturhist-mediz Vereins zu Heidelberg*, 1876, 1877, and 1878; *Liebig's Ann.*, 1878, vol. cxc, 228.

† *Phil. Trans. Roy. Soc. London*, 1884, 619. "The Conditions of Chemical Change in Gases."

after the production of steam can the carbonic oxide burn by means of a secondary reaction with the steam formed. This reaction is reversible, and therefore can be brought under the Guldberg-Waage law. Experiment showed, however, that for the law to be generally applicable to this case, it was necessary that (1) the temperature must be kept at such a height that all the water formed may remain in the gaseous state, and (2) that no more oxygen is added than is necessary for the formation of the water taking part in the change; for with excess of oxygen the reaction goes on in presence of a gas (oxygen) inert to the other three, CO, CO_2, and H_2O.

For the condition of equilibrium,

$$p\mathrm{CO}+p^1\mathrm{CO_2}+q\mathrm{H_2}+q^1\mathrm{H_2O},$$

the Guldberg-Waage equation was confirmed, and the constant found to be $k^2=4$, or,

$$\frac{p}{p^1}=4\frac{q}{q^1} \quad \text{and} \quad \frac{pq^1}{pq}=4.$$

It seemed of interest to investigate a second case of this equilibrium in mixtures of simple gases; therefore Dixon and myself began some preliminary experiments on the case of the distribution of hydrogen between oxygen and chlorine. This reaction had previously been studied by Bötsch. In his inaugural dissertation presented at the University of Tübingen in 1882, and published in *Liebig's Annalen* ccx, 207, he stated that when hydrogen mixed with oxygen and excess of chlorine is fired in a closed eudiometer no steam is formed in the combustion, but all the hydrogen is burned to hydrochloric acid. Schlegel, in 1884, working with an improved apparatus which avoided Bötsch's chief sources of error, extended the observations to hydrocarbons CH_4, C_2H_2, C_2H_4, and other bodies such as $(CH_3)_2O$, C_2H_5Cl, &c. He obtained a similar result. Bötsch's statement with regard to mixtures of hydrogen, chlorine, and oxygen, we found to be incorrect. Under the conditions under which he worked the quantity of water formed would, however, as is shown later, be certainly too small to be detected by the method he used. Our results are published in the *Manchester Memoirs*, 1890 [iv.], vol. iii.* When a mixture of 40 vols. hydrogen, 40 vols. chlorine, and 60 vols. oxygen are fired at the ordinary temperature and pressure, a contraction of about 10% is produced. This is chiefly due to the

* *See p.* 302.

formation of a considerable quantity of steam and the condensation with it of some of the hydrochloric acid produced at the same time. The amount of the steam found varies with the area of the cooling surface to which the gases are exposed in the explosion, and so with the shape of the particular vessel used.

After we had made a communication on our experiments to the British Association at Newcastle, in 1889, a paper by Messrs. Hautefeuille and Margottet appeared in the *Comptes Rendus*, 1889, and a second paper in the *Annales de Chimie et Physique*, vol. xx, 1890, in which the authors described experiments which agreed closely with our own. Their explosion vessel was, however, not heated to prevent condensation of the steam during the reaction—a precaution found to be necessary in the similar experiments with carbonic oxide, hydrogen, and oxygen. On account of other work our experiments were allowed to remain at this stage till I resumed them in the university laboratory of Tübingen, in 1891. Before proceeding to investigate a case of equilibrium such as this, it is necessary to study each of the several reactions which take place simultaneously in the explosion, and to ascertain whether these reactions are "direct"—that is, take place without the intervention of a third body. In this case the possible reactions are six in number.

(1) The synthesis and decomposition of water ..... $2H_2+O_2=2H_2O$ (1)
$2H_2O=2H_2+O_2$ (2)

(2) The synthesis and decomposition of hydrochloric acid. $H_2+Cl_2=2HCl$ (3)
$2HCl=H_2+Cl_2$ (4)

(3) The secondary reactions between the various products of combustion ..... $4HCl+O_2=2H_2O+Cl_2$ (5)
$2H_2O+2Cl_2=4HCl+O_2$ (6)

First Reaction: $2H_2+O_2=2H_2O$.

Dixon* has shown that the minimum pressure under which knallgas will explode is the same when dry as when saturated with aqueous vapour. It is thus probable that this reaction is a direct one.

* *Phil. Trans.*, 1884, p. 634. *See* also *Trans. Chem. Soc.*, vol. 188, p. 107.

Second and Fourth Reactions: Dissociation of H_2O and HCl.

As regards these reactions, it is known that the quantity of hydrogen left over in an explosion of this gas with excess of almost any other with which it combines, under ordinary circumstances in a eudiometer,* is exceedingly small, indeed is scarcely measurable.

It is also shown in the following series of experiments that no hydrogen remained over from the explosion, with the exception of the experiment No. 18, where the mixture contained a very large excess of diluent gas, and was very near the limit of explosibility. In this case it only amounted to $\frac{1}{10}$ c.c. The permanent dissociation of steam and hydrochloric acid may thus be considered as not taking place in these experiments.

Third Reaction: $H_2+Cl_2=2HCl$.

In the case of chlor-knallgas it was discovered independently by Pringsheim (*Annalen*, 1887, N.F., xxxii, p. 421), and Dixon and the author (*loc. cit.*), that the dryness of the mixture made a considerable difference in the combination of the gases by light. According to our experiments the mixture, when thoroughly dried by phosphoric anhydride, requires twenty-five times the amount of light to bring about its explosion as when saturated with moisture. On the other hand, we never succeeded in obtaining a mixture which could not be fired, even by a feeble spark, though in several experiments the drying was prolonged in the dark for several weeks. It is therefore probable that after the gases have once been raised by a spark to a high temperature, the reaction between hydrogen and chlorine proceeds directly. These conclusions with regard to $(2H_2+O_2)$ and (H_2+Cl_2) are also confirmed by recent work on the rate of propagation of the "explosion wave" in mixtures of these gases. In both cases aqueous vapour present only acts like any other inert gas, slightly *diminishing* the rate, and *not*, as in the combination of carbonic oxide and oxygen, playing an important part in the reaction. The numbers obtained were 1745 metres per second as the velocity for the dry gas,

* The words "in a eudiometer" are here purposely inserted because it was found by Dixon and Smith (*Manch. Lit. and Phil. Proc.*, 1888, vol. ii) that in the "explosion wave" an appreciable amount remained unburnt. In a very narrow eudiometer this is also the case.

while when saturated with aqueous vapour at 14° the mean number found was 1720.* For carbonic oxide and oxygen, on the contrary, the rate found for the well-dried mixture was 1264 metres, whereas when saturated at 20° it was 1703, an *increase* of about 30 %.

FIFTH REACTION: $4HCl+O_2=2H_2O+2Cl_2$.

This reaction represents the change on which is founded the well-known Deacon's process for chlorine manufacture. To see if it takes place at the temperature of the explosion, the following experiment was made. A mixture of equal volumes of hydrogen and oxygen was mixed by diffusion in a glass vessel with a known volume of dry hydrochloric acid gas free from chlorine. When thoroughly diffused the mixture was exploded by a spark, the products of combustion being driven out through potassium iodide solution by a current of air. About 3 % of the chlorine of the hydrochloric acid present was set free, showing that *at the temperature of the explosion, oxygen abstracts hydrogen from hydrochloric acid.*

SIXTH REACTION: $2H_2O+Cl_2=4HCl+O_2$.

The last reaction was tested in the following way. A strong bulb of glass, provided with a narrow graduated U-tube gauge containing boiled oil of vitriol, was one-third filled with distilled water. Chlorine was then passed in for two hours through the water, the bulb being meanwhile heated to about 80° C., at which temperature the tension of the aqueous vapour present is approximately equal to that of the chlorine. The apparatus was so constructed that no absorption of chlorine or HCl could take place at the surface of the H_2SO_4, which was separated from the gas in the bulb by a column of nitrogen. The air bath used to heat the bulb could be considered as perfectly constant during the short time the experiment itself lasted. The chlorine stream being interrupted and the inlet tap closed, strong sparks from a large induction coil, intensified by a Leyden jar, were passed through the mixture by means of platinum-iridium wires. A rise of 10 mms., corresponding to a diminution of pressure of about 0·2 %, took place after sparking the mixture for four minutes. This

* These are the *corrected* numbers.—H. B. D.

diminution, which arises from the absorption by the water of the hydrochloric acid formed, is proportional to the time of sparking. In half an hour an absorption of 3 or 4 % can readily be obtained. *Chlorine and aqueous vapour are therefore capable of reacting at a high temperature, giving hydrochloric acid and oxygen.*

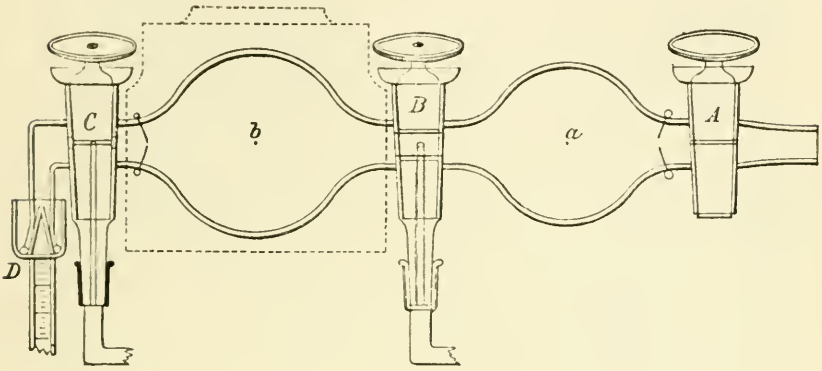


FIG. 1.

METHOD OF THE RESEARCH.

The method I at first attempted to use for making, exploding, and analysing mixtures of hydrogen, chlorine, and oxygen was that briefly described in the above-mentioned paper (*Manchester Memoirs* [iv.], vol. iii., 1890). The apparatus, shown in Fig. 1, consisted of two bulbs of thick glass, holding 180 and 140 c.c. respectively, each of which was provided with firing wires of platinum-iridium. The bulbs can be connected by means of the three-way tap *B*, having its straight bore very wide (10 mms.) to allow of rapid diffusion. The smaller bulb *a* is closed at its other end by an ordinary tap *A*, and the larger, by means of a three-way tap *C*, can be put into communication either with the air, or a tube 600 mms. long, which is graduated into millimetres, and bent down at right angles to the axis of the bulbs, so that it stands in a vertical position. One bulb is then filled by displacement with the mixture of hydrogen and oxygen in the required proportions, and the other by chlorine, the bulbs being shut off from one another, and both at atmospheric pressure. The space between the three-way tap *C* and the surface of the liquid in the barometer tube (sulphuric acid or mercury) remains during the whole experiment

filled with air, or other inert gas, and, consequently, no absorption of chlorine can take place in this tube. The bulbs are then put into communication for some hours in the dark, and then, after the temperature and pressure have been read, the gases are fired by a spark from an induction coil. The contraction is then determined by the rise of the mercury in the barometer tube, which occurs on opening the tap *C* to connect the gauge with the bulbs, after they are cooled to atmospheric temperature.

After finding that a division of the hydrogen between the chlorine and oxygen really takes place, the next step was to repeat the experiments under such conditions that no condensation of the steam formed could occur during the explosion. This apparently simple problem offered, however, very many experimental difficulties. The first method tried was to heat the larger of the two bulbs *b* in an air bath to about 110°, and explode at that temperature. For this purpose a rectangular air bath was constructed so as to completely surround the bulb, the two tubes leading to the taps projecting about 1 cm. on each side through holes in the walls of the air bath. The difficulty consisted in getting these two tubes to the right temperature. If too cold, water condensed during the explosion, and the whole experiment was worthless. If, on the other hand, they were made hot enough to prevent condensation by being wrapped with sheet asbestos, it was not possible to prevent a leakage of the taps, due to the effect of heat on the lubricant. The taps were of the specially good workmanship of F. Müller of Bonn, and were from time to time carefully reground. Many lubricants, including sulphuric and syrupy phosphoric acids, were tried, but without success. This method of mixing the gases by diffusion, which had also the disadvantage that it took about twelve hours for completion, was accordingly given up.

After many further experiments, which it is not necessary to describe, the following apparatus (Fig. 2), though possessing the disadvantage of being somewhat complex, was found to answer the required purpose. *A B* is a eudiometer of strong glass, having firing wires of platinum-iridium. This alloy is much less easily attacked by chlorine than pure platinum. The eudiometer could be heated to a uniform and constant temperature by a small vertical air bath on the principle described by Prof. Lothar Meyer, in *Berichte der Deutschen Chem. Ges.* xvi, *a* 1087. It consists of

three concentric cylinders, between which the products of combustion from a ring burner circulate up and down, maintaining in the middle a constant temperature, and escaping through the perforated lid covering the upper aperture. The capillary tube of the eudiometer passes out through the lower opening, which is

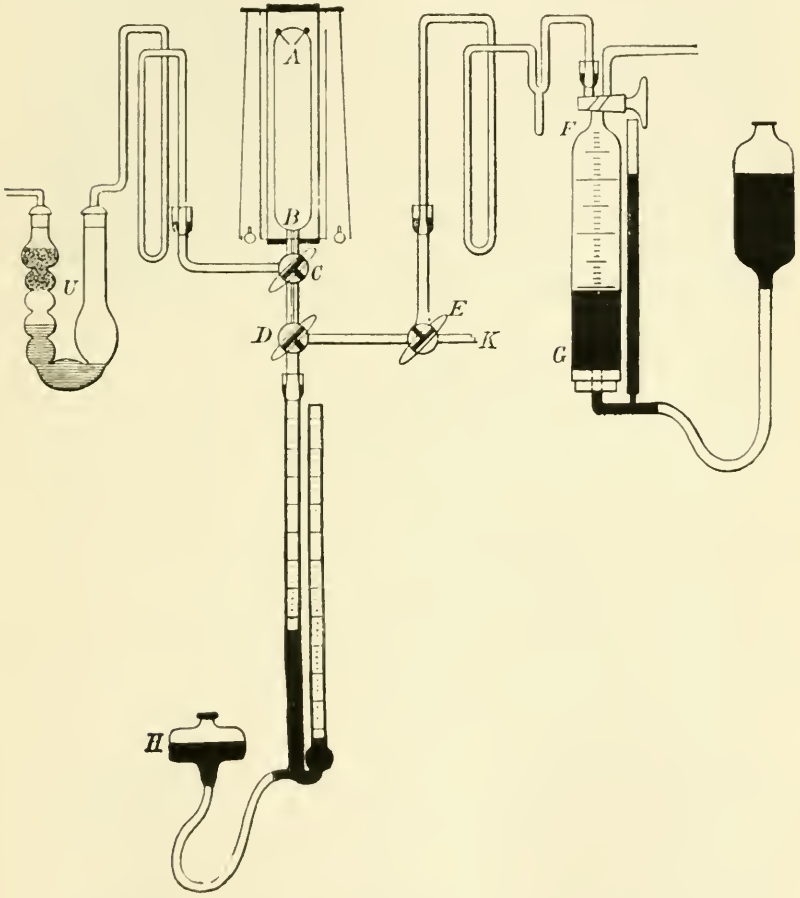


FIG. 2.

closed by two semicircular doors, working on pivots. As it was desirable to have the same temperature in the air bath in all the experiments, and as this is, under ordinary circumstances, not easy to adjust, the following arrangement was made for the purpose. The gas supplying the burner was passed through a Moitessier's glycerine gas regulator, which kept the pressure

constant, then through a tap provided with a long pointer moving on a scale graduated into degrees. A table was made once for all of the temperatures reached in the air bath with the particular burner used, when certain weights were on the regulator, and when the tap was adjusted to a certain angle. It was thus easy to obtain any constant temperature required in a very short time. To the lower end of the eudiometer, which, in most cases, had a capacity of 55 to 60 c.c., was fused the capillary three-way tap *C*. One branch of this tap communicated with a **U** tube containing potassium iodide solution, and through this with the air pump; and the other with a second three-way tap *D*. The vertical branch of *D* was connected by means of a carefully ground glass joint with a double-limb manometer, 800 mm. long, and having both limbs graduated into millimetres. By means of a side piece and flexible tubing, communication could be made between this

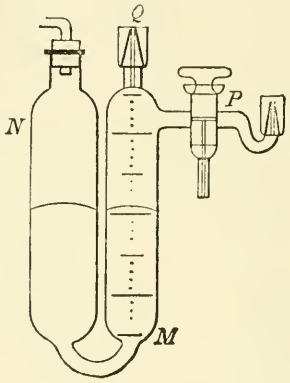


Fig. 3.

and a vessel containing mercury, which could be firmly clamped at any height. Since, in each experiment, the pressure of the gas let into the eudiometer had to be adjusted, this mercury reservoir was purposely made very wide, so that the level of the mercury in it remained almost unaltered. With this form of manometer no correction for capillarity is required, since the meniscus in each limb is of the same form. The readings were made with a telescope at a distance of one to two metres. The horizontal branch of tap *D* leads to a third tap, through one limb of which the hydrogen and oxygen mixture is brought in, while the other serves as outlet for chlorine. To the same glass joint to which

the manometer was fitted, was ground the upper part of the vessel shown in Fig. 3, used to collect and measure the chlorine. This consisted of a U-shaped tube, *M N*, having an inlet tube with tap *P*, and both limbs graduated into millimetres. The tube *U*, in Fig. 2, 200 mms. long, and provided with six bulbs, contains about 8 c.c. of a saturated solution of potassium iodide, and in the upper bulb, on the side nearer the pump, a few pieces of solid potassium iodide, moistened with water. The tube so arranged was found to work admirably, and no experiment was lost through failure of this to absorb all the residual chlorine. In the earlier experiments a Sprengel air pump was used to pump out all the residual gases, but this was afterwards changed for one of the Toepler pattern, which did its work in a much shorter time. The preliminary evacuation was always made with a good water pump of the form described by von Babo, with which a pressure of about 20 mms. could easily be reached.

Preparation of the Gases.

The mixture of hydrogen and oxygen was prepared by electrolysis and stored in the apparatus represented in Fig. 4. The

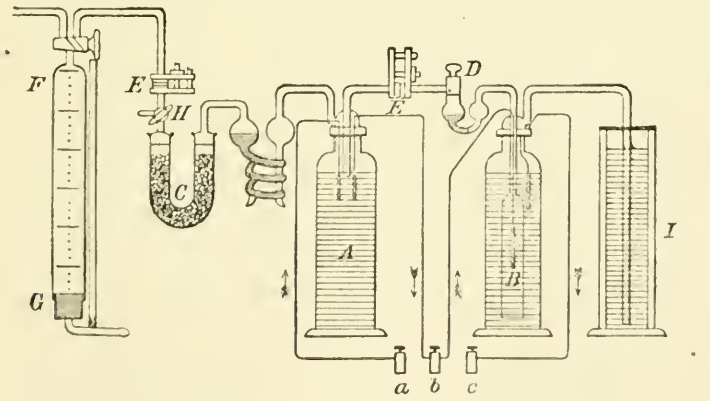


Fig. 4.

Dreschel's wash bottle *A*, having ground delivery tubes, the longer of which reaches just below the neck, is provided with platinum electrodes in communication with the binding screws *a* and *b*. To the longer delivery tube of the similar vessel *B*, is fused a wide bell-shaped tube, reaching almost to the bottom. Through the stopper of this bottle is fused in the same way a second pair of electrodes,

one being in the upper part of the bell, and the other outside it. These electrodes are in communication with the binding screws *b* and *c*. The gas generated in the bell passes through the small washing apparatus *D*, and is then mixed with that evolved from *A*. For the connection of the various parts of this and other apparatus, without the use of india-rubber, the glass joints invented by Prof. von Babo, and shown in Fig. 5, and at *E E*, were found very convenient. They consist of two circular ground-glass plates

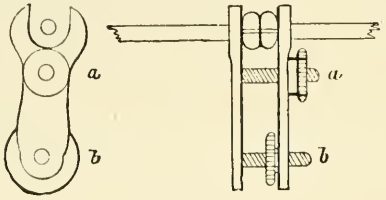


FIG. 5.

pierced in the centre each with a small hole and fused to the glass tubes to be connected together. The plates are greased with a little fat and then pressed together by means of the small brass clamps provided with two nuts, *a* and *b*, shown in Fig. 5. The great advantage of these joints is that *any* two tubes so fitted can be connected together, while with the ordinary joint only the particular ones which have been ground to one another.

The apparatus for drying the gas consisted of a small Winckler worm with H_2SO_4 and a **U** tube filled with pumice moistened with boiled sulphuric acid. Hence the gas passed by a tap either out into the air or was collected in the pipette *FG*, filled with mercury. On the surface of the mercury were several pieces of fused potash, which served to free the gas from any trace of acid spray it might contain. In the whole of the generating apparatus there were no india-rubber connections where diffusion could take place. Where possible the parts were fused together, and where this was inconvenient, they were connected by ground-glass joints. The apparatus thus once filled with gas, required only to be kept shut off from the air, when not in action, no diffusion of the hydrogen taking place. By connecting the poles of a battery of seven small accumulators with the screws *a* and *b*, a mixture of $(2H_2+O_2)$ could be obtained; or, by connecting *a* and *c*, a mixture of either $(4H_2+O_2)$ or (H_2+O_2), the latter being the one most

suited to these experiments. The unused gas, in the latter case hydrogen, passed out through a column of water in the cylinder *F*.

Chlorine.

It was necessary for these experiments to have dry chlorine free from air and free from hydrochloric acid. Many methods with as many different forms of apparatus were tried to attain this end, but without success. The gas, when made from manganese dioxide, even after previous boiling of the manganese with dilute hydrochloric acid, is extremely difficult to free from air. Large quantities of material are required to drive out the air completely from comparatively small apparatus, and the whole method is tedious and uncertain. Bunsen's method of preparation from

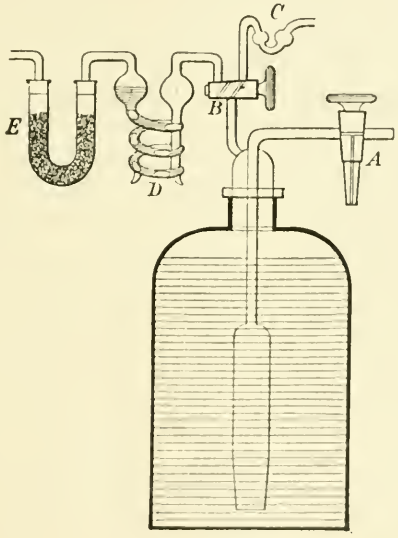


Fig. 6.

potassium bichromate and hydrochloric acid gives chlorine free from air, but only in comparatively small quantity and with much hydrochloric acid, which must be removed by washing with water and copper sulphate solution. From a proposal made to me by Professor Beilstein, I have been able to work out a practical and convenient method of preparing pure chlorine on a tolerably large scale. He suggested to me the use of chlorine hydrate. The following apparatus (shown in Fig. 6) was found to answer the

purpose admirably, and in it about two hundred litres of gas could easily be condensed and stored. The receptacle consisted of a strong narrow-necked bottle, holding about two to three litres, and filled almost to the neck with distilled water, from which the air had been expelled by boiling. To the neck was ground a hollow stopper provided with two tubes, one of which was wide and bell-shaped, reaching to the bottom of the bottle. To this, which formed the inlet tube, was fused a three-way tail tap *A*, and to the outlet a second tap *B*. One limb of the latter led to a small bulb apparatus containing about 1 c.c. water, and the other to the drying apparatus, which was fused to it. This consisted of a small Winckler worm with sulphuric acid and a U tube with ground necks filled with pumice moistened with sulphuric acid. When not in use, the end of this tube was closed by a small cork. The bottle was cooled to 0° by surrounding it with pounded ice. A lower temperature must not be used, since in that case the inlet tube is immediately stopped up. The chlorine was evolved in a large flask from the mixture recommended by Klason (*Berichte der Deutschen. Chem. Gesellschaft*, 1890, page 334), consisting of 900 parts by weight of common salt, 400 of manganese, 1,200 of sulphuric acid, and 600 of water. This mixture possesses the great advantage of giving off the chlorine at a very low temperature in an exceedingly steady stream, lasting many hours. The gas first passed through an efficient washing apparatus to free it from hydrochloric acid, then to a condensing vessel through a long glass tube flexible enough to allow the bottle to be shaken, and out to a stone vessel filled with alternate layers of lime and charcoal, by the tube *C*, which contained a few cubic centimetres of water in order to show how much of the gas was being absorbed. Usually after the current had passed for half an hour, very little escaped from the bottle, except the traces of air still remaining in the gas. The hydrate Cl_2, $10H_2O$ forms first as a foam, which consists of the pellicles of floating bubbles of chlorine. During this stage the bottle must be shaken violently about once every ten minutes to bring this foam down again into the water. After another hour the hydrate forms as crystals, which remain in the liquid, and the process requires no further attention. At any temperature below 9° C., the chlorine can be stored in this form very conveniently. It is only necessary to set the bottle in warm water

to obtain a stream of pure chlorine, which can be regulated with ease. After running for only ten minutes, the dried gas evolved in weak diffuse daylight contains generally less than 0·2% of impurities unabsorbable by potash. Direct titration of the quantity of chlorine contained in a vessel of known contents filled from this apparatus, showed that the gas contained no hydrochloric acid. In performing this experiment it is essential that the vessel used—best in form of a cylinder—be filled from below and have its exit above. If the air be displaced from the tube in a horizontal position, the heavy chlorine creeps along the bottom, and the last traces of air floating above it take several hours for removal by simple diffusion. To obtain chlorine by this process absolutely free from other gases, especially oxygen, it is essential that the evolution from the hydrate take place in the dark. In a clear atmosphere, especially in summer, the action of daylight is quite evident. On one occasion, in strong sunlight, I have collected 20 c.c. oxygen from a flask containing chlorine water in twelve minutes.

The carbonic acid was made in a Muencke's apparatus (*Dingl. Pol. Journ.* cdxcvii, 1884), which gives it exceedingly pure, and allows the easy removal of the spent hydrochloric acid without letting in air.

Analysis of the Chlorine.

For estimation of the air or other impurities in carbonic acid or chlorine, the apparatus shown in Fig. 7 was used. *A B* is a cylinder holding about 40 c.c., having a narrower part between *A* and *C*. The volume between the taps is ascertained once for all by weighing out with mercury, and the part *A C* is provided with a graduated paper scale reading off directly the percentage vol. from 0·5% downwards. The tap *C* is an ordinary three-way, and *B* a four-way, having the bore of the plug in the form of two radii at right angles to one another. The U shaped vessel containing potash solution is fused to one tube, and the other is connected by india-rubber with a reservoir containing water. The apparatus is used as follows: The cylinder is filled with water from *F*, and the potash solution is brought into the U tube, filling it up to the tap *B*. The gas to be analysed is passed through the horizontal tube *C*. The reservoir *F* is lowered, communication having been

established between F and the cylinder, and the tap C opened, till the cylinder is full of gas, which is at once shut off. B is then

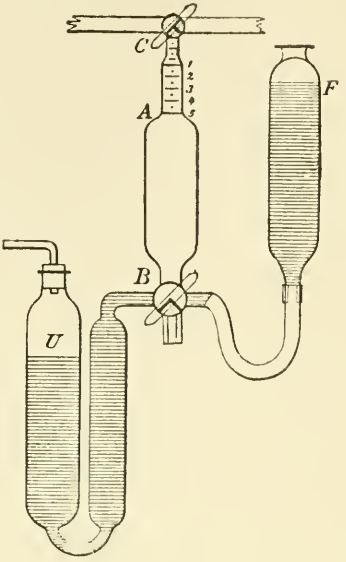


Fig. 7.

turned through 90°, and by gentle pressure from the mouth, applied by means of a tube attached to U, a little potash is forced up into

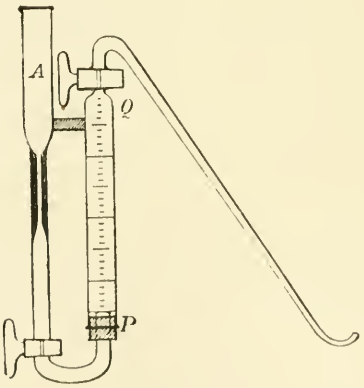


Fig. 8.

$A\,B$, into which it spontaneously further rises as the gas is absorbed. When the absorption is complete, B is again turned back and the gas measured under atmospheric pressure. The potash is run

back, the walls of the cylinder washed with water from F, which is afterwards run out at B. The reservoir is filled again, and the apparatus is ready for another estimation. With this apparatus there is no liberation of dissolved air from the absorbent liquids, since the pressure on the liquids remains practically the same the whole time.

Measurement of the Oxygen.

The first series of experiments made with (H_2+O) and varying quantities of chlorine, although the results obtained were not otherwise satisfactory, showed that the quantity of oxygen burned in the explosion was extremely small. Now, as the quantity of oxygen left over was always determined as a control of the chlorine determination, it was necessary that the measurement be made with extreme accuracy, otherwise it had but little worth. The method adopted was to collect the oxygen in a tube of the form shown in Fig. 8, in which was about 5 c.c. of strong potash solution. By means of mercury from the reservoir A attached to P, the gas could be transferred into the eudiometer of a Lothar Meyer gas-analysis apparatus, and measured under diminished pressure. As shown in the paper describing this apparatus (*Journ. Chem. Soc.* xlv, 581), the error of measurement reaches a minimum when the number of eudiometer divisions (millimetres) is equal to the pressure on the gas in millimetres of mercury.

Measurement of Chlorine.

The chlorine was absorbed by saturated potassium iodide solution in the bulb tube previously described, and titrated with $\frac{1}{50}$th normal sodium hyposulphite. The burettes used were controlled by the exceedingly convenient little apparatus of Prof. Ostwald (*Journ. Prac. Chem.*, vol. xxv, 452), and, where necessary, the correction applied.

Method of Experiment.

The apparatus being all dried with exception of the tubes leading to the pump, the experiment was performed as follows. First, communication was established between the pump, eudiometer, and manometer up to the tap on the (H_2+O_2) pipette, and these parts were exhausted as far as possible. Owing to the

water necessarily present in the potassium iodide tube, a tension of 15 mms. generally remained. When, however, the pump was worked quickly, it was often possible to go about 5 mms. below the tension of aqueous vapour at the temperature in question. During the exhaustion the electrolysis was set going, and the (H_2+O_2) pipette filled with gas. The tap C was now turned so as to shut off the pump, and (H_2+O_2) let into the eudiometer up to atmospheric pressure; this gas was pumped out, and the filling repeated. After a third evacuation the pump was shut off from the eudiometer, and pure (H_2+O_2) let in up to the pressure required, which was read off with a telescope on the manometer below; the temperature of the gas also being noted. Taps C and D were then closed, and the manometer taken away. The chlorine holder, half filled with concentrated pure sulphuric acid, was then clamped to D; by means of a rubber tube attached to N, closed by a pinch cock, the acid in the limb M was brought up nearly to the level of the tap P. The glass joint on P, and the one on the drying tube of the chlorine apparatus, were now connected by a flexible glass tube, and a current of chlorine driven in through P, and out along the horizontal tube DEK to the analyser described. As soon as the gas was pure the tap D was closed, the acid allowed to fall in M, which was thus filled with pure chlorine, N being left open to the air. The short capillary tube CD, which contained (H_2+O_2), was now exhausted by turning the tap C, so as to put CD in communication with the exhausted pump reservoir. Taps C and D were then so turned that part of the chlorine in M was sucked up into the semi-vacuous eudiometer, which was in complete darkness. Before any diffusion of (H_2+O_2) could take place they were closed again, and the difference in height of the H_2SO_4 in the two limbs was read off. The specific gravity of the sulphuric acid being known, this height could be reduced to millimetres of mercury, and added to or subtracted from the barometric pressure, giving the total pressure of gas in the eudiometer. This being shut off, a current of carbonic acid, which from analysis contained in most cases less than $\frac{1}{10000}$ of impurity, was now passed through $KEDC$ and to the pump, displacing the 15 mms. of (H_2+O_2) which remains in this part. While the tubes from C to the pump are being completely filled with CO_2, and exhausted as far as possible, the air bath is heated

to about 115° C. and the explosion made. The oxygen tube is now put over the delivery tube of the pump, and the tap *C* very slowly opened. The chlorine and hydrochloric acid are absorbed in the U tube, and a mixture of residual oxygen with carbonic acid passes on, and is collected. When pumped out as far as possible, carbonic acid is let into the still hot eudiometer to about half an atmosphere pressure, and again pumped out, bringing with it the residue of gases that remained from the first exhaustion. After repeating this, no measurable residue, other than carbonic acid, remained in the eudiometer.

The U tube is then washed out, and the solution titrated with sodium hyposulphite ; the oxygen is transferred from the collecting tube to the gas-analysis apparatus, and after two or three hours its volume read off. In many cases a complete analysis of the oxygen was made by exploding with hydrogen. This showed whether any hydrogen remained over from the explosion. In only one instance, Expt. 18, was any hydrogen found in the analysis. As it was desirable to vary the pressure under which the mixture was fired, an arrangement for reducing this below the atmospheric pressure was made as follows : A large bottle having a ground stopper provided with two tubes, one of which leads to the bottom of the bottle, was connected by a three-way tap with a manometer and vacuum pump. The pressure in this was reduced during the warming of the eudiometer to a trifle below what was desired in the explosion, and as soon as the air bath had become constant the pressure in the eudiometer was equalised with that in the bottle, with which it was connected by a short piece of strong rubber from the tap *D*. The chlorine which escaped was not allowed to come into contact with the mercury in the gauge, since it remained at the bottom of the bottle, which holds at least 10 litres, till the reading of the pressure was made, after which it was immediately driven out by a stream of air.

Results.

The results of all the experiments are given in the following table, and the accompanying diagram, Fig. 9, in which the abscissæ represent quantities of chlorine in the mixture, and the ordinates hydrochloric acid formed.

In all these experiments the quantity of oxygen used was equal

to the hydrogen, and the sum of both was for convenience sake always called 100 vols., the quantities of chlorine added varying from 10 to 95 vols. It was not possible to study the effect of variations in the proportion of oxygen, since, if it was diminished

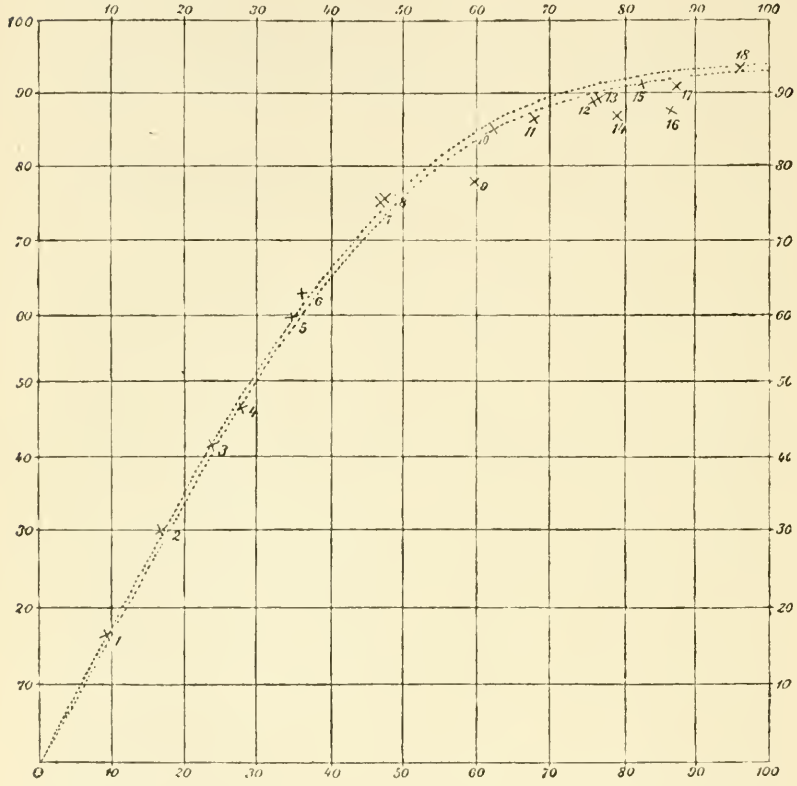


FIG. 9.

to half the hydrogen, the quantity of steam formed became so small, and the error of its determination so proportionally large, that no conclusions could be drawn from the experiments,* while on the other hand, if the oxygen were increased, the limits of explosibility were soon reached. Putting, then, $H_2+O_2=100$, the

* In my experiments with hot eudiometer, less steam is formed than in the series made by Messrs. Hautefeuille and Margottet, in which they were able to use H_2+O

diagram, Fig. 9, shows the increase in the quantity of the hydrochloric acid formed in the different experiments with increasing chlorine.

Consideration of the Individual Experiments.

Dixon has shown that in cases of this kind, the pressure under which the gases are fired exerts an influence on the relation K^2, but that beyond a certain crucial pressure, this influence becomes less than the experimental error. As a *determination* of this particular pressure would necessitate many special experiments, and would possess, moreover, comparatively little interest, I thought it desirable to make all the experiments at a high pressure, and only determine whether a variation of pressure somewhat greater than might occur accidentally in a series of experiments, made any alteration in the relation. It was found, however, that with mixtures containing less than about 70 parts of chlorine to 100 H_2+O_2, the pressure developed in the explosion was so high that the eudiometer was generally broken. Accordingly, after making the experiments numbered 7, 8, 9, 10, 11, 13, 16, 17, 18, at about 1000 mms. pressure, experiments 12 and 15 were made at atmospheric pressure, showing that within the limits of experimental error, an alteration of pressure from 1000 to 720 mms. makes no difference in the relation. Experiments 5 and 6 were now made at atmospheric pressure. On further reducing the quantity of chlorine present, the same difficulty with the eudiometer was again encountered, and it was evident that if the series was to be completed, a further reduction of pressure would be necessary. Comparative experiments were again made to see if this was allowable, and on this proving to be the case, experiments 1, 2, 3, and 14 were made at a pressure of somewhat over 500 mms. In experiment 4, which was the last, the eudiometer was risked at 1000 mms., and did not break. The result seemed to show that in this case the *doubling* of the pressure has no influence. The experiments could not be carried further in the other direction—that is, with more chlorine than 95 vols., since in experiment 18 the explosion was extremely weak, and traces of hydrogen remained unburnt.

In order to see if the Guldberg-Waage law holds for these experiments, the quantities of HCl which should be formed with

quantities of Cl varying from 10 to 100, was calculated in the following way. For a general case this is done as follows: Let the quantities of H_2+O_2 each $=P$, and the varying quantity of $Cl=Q$, and let the state of equilibrium be represented by the equation :—

$$pO^2+p^1H_2O+qCl_2+q^1HCl.$$

From the Guldberg-Waage relation we then have :—

$$K^2=\frac{p}{p_1}\times\frac{q^1}{q}. \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

Also

$$p+\tfrac{1}{2}p^1=P \quad \ldots \quad \ldots \quad \text{(Oxygen)} \quad (2)$$
$$p^1+\tfrac{1}{2}q^1=P \quad \ldots \quad \ldots \quad \text{(Hydrogen)} \quad (3)$$
$$q+\tfrac{1}{2}q^1=Q \quad \ldots \quad \ldots \quad \text{(Chlorine)} \quad (4)$$

By eliminating from (1) p, p^1 and q we get $K^2=\dfrac{(2P+q^1)q^1}{(2Q-q^1)(2P-q^1)}$

Solving this quadratic for q^1 we get

$$q^1=\frac{P(1+K^2)+K^2Q\pm\sqrt{[P(1+K^2)+K^2Q]^2+(1-K^2)4K^2PQ}}{(K^2-1)}$$

The mean of one or two experiments gave $K^2=25$ nearly; so in order to see how the experiments agreed with the theory, the whole curve representing the variation of the hydrochloric acid with the chlorine was calculated for $K^2=25$. Setting this value and $P=50$ into the above equation and simplifying, it becomes :—

$$q^1=\frac{1300+25Q\pm\sqrt{(1300+25Q)^2-120{,}000Q}}{24}$$

In this, the values for Q from 10 to 100 were substituted. The lesser root, that is the one with the $-$ sign, is the only one possible in this case. Since the curve, the upper one on the diagram, agreed pretty well with the mean of the observations, the value of K^2 was then calculated for each experiment. The results are shown in the following table. From the well-known formula,* the probable error of the mean of the whole and of a single observation was calculated, giving for the former 0·6, and the latter 2·6.

* See Stewart and Gee, *Practical Physics*, vol. i, or Kohlrausch, *Leitfaden der practischen Physik*.

TABLE.

No. of Expt.	K^2	Deviation from Mean.	$\left(\text{Deviation from Mean}\right)^2$
1	28·8	+5·8	33·64
2	27·6	+4·6	21·16
3	23·3	+0·3	00·09
4	20·4	−2·6	6·77
5	20·1	−2·9	8·47
6	26·7	+3·7	13·69
7	26·2	+3·2	10·24
8	26·1	+3·1	9·61
9	15·6	−7·4	54·76
10	29·0	+6·0	36·01
11	21·9	−1·1	1·21
12	22·6	−0·4	0·16
13	22·5	−0·5	0·25
14	16·2	−6·8	46·24
15	22·4	−0·6	0·36
16	19·4	−3·6	12·96
17	20·0	−3·0	9·00
18	25·2	+2·2	4·84
	Sum = 414·0	8 values > 23·0	269·48 = 8
	Mean = 23·00	10 values < 23·0	

Probable error of mean of whole $= \pm 0{\cdot}6745\sqrt{\dfrac{269{\cdot}48}{17\times 18}}$

$= \pm 0{\cdot}607$

Probable error of a single experiment $= \pm 0{\cdot}6745\sqrt{\dfrac{269{\cdot}48}{17}}$

$= \pm 2{\cdot}577$

$\therefore\ K^2 = 23{\cdot}00 \pm 0{\cdot}607.$

An attempt was made to compare the experiments with the law in another way, as follows: By differentiating the equation $K^2 = \dfrac{q^1(2P+q^1)}{(2Q-q^1)(2P-q^1)}$, setting $\dfrac{dK^2}{dQ} = 0$, and simplifying, we get a value for $\dfrac{dq^1}{dQ}$ viz.:—

$$\frac{dq^1}{dQ} = \frac{2Q}{q^1} + \frac{2}{P\left[1-\left(\frac{q^1}{2P}\right)^2\right]}$$

Now, by substituting in this equation the value for Q and the corresponding q^1 for each experiment, we get a series of values for $\frac{dq^1}{dQ}$, which should agree with those calculated from the experiments.

For example, if Q, as in Expt. (2) = 30·63, then $\frac{dq^1}{dQ}$ calc. = 1·79.

For Expt. (2) $\frac{dq^1}{dQ}(1 \rightarrow 2) = \frac{13{\cdot}26}{7{\cdot}28} = 1{\cdot}82$

and $\frac{dq^1}{dQ}(2 \rightarrow 3) = \frac{11{\cdot}96}{7{\cdot}20} = 1{\cdot}66$

The mean of these, which is the true value for dq/dQ in Expt. (2), is 1·74, which agrees fairly well with the calculated value 1·79. The values found by this method agree tolerably well with the calculated when Q is very small and also when it is large, that is, when q^1 approaches 2Q and 2P respectively; but in the middle the agreement is much worse.

The conclusion, then, from these experiments is :—

(1) If to a mixture of oxygen and chlorine, hydrogen insufficient to combine with both be added, and the mixture exploded, a division of the hydrogen between oxygen and chlorine takes place ; and

(2) The quantity of each of the products of combustion formed, provided they remain within the sphere of action, is such that the number of molecules of hydrochloric acid, multiplied by that of the oxygen, divided by the number of molecules of steam, multiplied by that of the chlorine, is a constant quantity, which in this case = 23·00.

In conclusion, I must express my sincerest thanks to Profs. Lothar von Meyer and Harold Dixon for the kind help and advice given to me in this work, and to the Government Grant Committee of the Royal Society for aid in procuring the required apparatus.

THE DURATION OF CHEMICAL ACTION IN THE EXPLOSIVE COMBINATION OF GASES.

By G. S. Turpin (*Bishop Berkeley Fellow at the Owens College*).

Preliminary Essay on the Conduction of Electricity by Gases.

WE are still far from a clear mechanical theory of the passage of electricity through gases, but of late some important advances towards the solution of that problem have been made, and as the latter part of this paper assumes the truth of a particular hypothesis based upon recent work in this direction, it seems well to give a brief discussion of the question as a preliminary to the consideration of the subject proper of my essay.

It has long been known that whereas gases at ordinary temperatures are practically perfect insulators for differences of potential below certain limits, on the other hand, hot gases, and especially flames, are able to conduct electricity, however small the E.M.F. between the electrodes. Until quite recently the experiments on hot gases had not been extended beyond the ordinary simple gases; E. Besquerel, and, later, Blondlot, showed that air begins to conduct slightly at about a red heat, and that the conduction does not exactly follow Ohm's law; Hittorf and others proved that mercury vapour at 360° does not conduct, an observation which is of special importance. J. J. Thomson has quite lately investigated a large number of gases and vapours, and finds that while air and most simple gases possess only very slight conductivity even at a yellow heat, other gases have comparatively enormous conductivities, and these gases are those

which are in a state of dissociation at the temperature of experiment. The exceptions are mercury vapour and steam at 1500°, which do not conduct although in a state of dissociation, but these may be explained by the dissociation being complete in the case of mercury, and by the absence of free atoms in the case of steam. We are thus led to the conclusion that gases conduct but feebly even at high temperatures unless we have chemical action attended by the production of free atoms taking place. The case of mercury vapour shows (*see*, however, J. J. Thomson, *Phil. Mag.*, May and June, 1890) that the presence of free atoms is in itself not sufficient, and the non-conductivity of steam at 1500° shows their presence to be necessary. Conduction in flames can be explained without introducing any additional qualifications; the oxyhydrogen flame conducts, though steam at 1500° does not, because we have in the flame the incessant decomposition of molecules, so that free atoms are always present, though any individual atom soon contrives with some other atom to form a molecule. The only difficulty in this connection is to explain the observations of Giese (*Wied. Ann.* xvii, pp. 1, 236, 519, especially §§ 54-61), which show that not only the flame itself conducts, but also the products of combustion issuing from the flame, though their conducting power is very small and rapidly diminishes with the time. These observations prove that the abnormal condition brought about by the process of combustion reverts only gradually to the normal. Giese himself supposes that free ions bring about conduction in flames, and, therefore, that the products of combustion still contain an excess of free ions above the small proportion corresponding to their temperature. The hypothesis here developed considers the presence of such ions to be insufficient, and points to the somewhat improbable conclusion (differing but slightly from Giese's) that in the burnt gases a few molecular disruptions are still occurring; in fact, that chemical action is not yet complete. It must be observed that Giese's method of experiment is extremely delicate.

Gases become conductors under other influences besides that of a high temperature associated with molecular disruptions, viz., under the influence of the electric discharge. Schuster and Arrhenius have found that a gas through which an electric discharge is passing is endowed with conducting power even for

the smallest E.M.F. But here, too, we have molecular disruptions taking place associated with a low average temperature of the molecules.

The essential condition for electrical conductivity in gases is, then, the occurrence of molecular disruptions, and that is also the state favourable to luminosity in gases. Hittorf and Siemens have shown that the luminosity of ordinary gases, even at very high temperatures, such as those of melting iridium, or of a Siemens regenerator, is very small, whereas many flames (in which no solids are present) are very bright though their temperatures are lower than those mentioned, and under the influence of the electric discharge gases become luminous at very low temperatures. The effect on luminosity may be attributed to the oscillations of the electric charges of the atoms set up by the rapid separations, and it is not impossible that these electric oscillations may influence the power of the atoms to bring about conduction, though it is not clear what would be the precise mechanism of such action.

Another cause which might possibly condition electric conductivity in gases is the electrification of the atoms induced by the disruption of the molecule in an electric field. Such charges must be induced if the atoms constituting the molecule were in electrical contact, and though the phenomena of electrolysis show that the atoms in a molecule may possess unequal or opposite electrifications, having regard to the complex structure of the atoms made evident by their properties, it does not seem impossible that they may be in one respect in electrical contact without the fixed atomic charges being divided. A rough calculation shows that the magnitude of the effect would be sufficient to account for the observed conductivities, provided the capacities of the atoms are much larger than those of conducting spheres of the same size, and the frequencies of the electrical oscillations of the atoms indicated by the vibration frequencies of the light emitted by them point plainly to the truth of that supposition. It seems not improbable that this same effect of charges induced by the electric field on the parts into which a molecule is decomposed might explain the observations of Boguski (*Zeitschrift für physikalische Chemie*. v, 69) on the variation of the electrical resistance of N_2O_4 with change of temperature. He found that on treating liquid

N_2O_4 the resistance undergoes a "dynamical" decrease while the temperature is rising, but when the temperature has become steady the resistance is greater at the higher temperature. This dynamical decrease of resistance is only observed between the limits of temperature within which the dissociation of N_2O_4 into $2NO_2$ is completed.

The further development and examination of this hypothesis, which is advanced with all reserve, lies beyond the scope of the present paper. It is enough that experiment has shown that in gases electrical conductivity is considerable only when molecular disruptions are proceeding in them, attended by the presence of free atoms, and in particular that the flame of H_2+O conducts while steam at 1500° does not.

The question whether the electrical resistance of flames and hot dissociated gases obeys Ohm's law has been answered in the affirmative by Hoppe for flames, and by J. J. Thomson for hot gases. Their experiments were not carried to any great degree of accuracy, and Blondlot showed that hot air does not follow Ohm's law exactly, but the deviations for the better conducting flames and gases are at any rate small.

The Duration of Chemical Action in the Explosive Combination of Gases.

It has been shown by Mallard and Le Chatelier that the propagation of flame in an explosive mixture of gases may occur in three different ways, which they entitle uniform propagation, vibratory propagation, and propagation by the explosive wave. In the first of these the flame moves with a uniform slow velocity which varies in different mixtures from 1 to 20 metres per second; in the régime of vibratory motion the flame oscillates rapidly, but progresses forward on the whole; and in the explosive wave the velocity is again uniform, but is very high, being measured in thousands of metres per second. In the first period the combustion is propagated by conduction of the heat of the flame to the adjoining layers, while the vibrations are set up in consequence of the temporary expansion produced by the act of combustion. In the explosive wave the velocity of the flame is nearly the same as the velocity of sound at the highest temperature produced by the explosion, and the combustion is propagated by a sound-wave so

intense that the adiabatic compression is sufficient to raise the temperature of the gas above the temperature of ignition. The definiteness of the velocity of the explosive wave (it is independent of the material and diameter of the tube, if not too narrow) makes its investigation extremely interesting, and a considerable mass of work has been done on the subject by Berthelot in France and by H. B. Dixon in England.

The limiting velocity of propagation corresponding to the explosive wave is not reached at once, but only after a period of development which has not yet been properly investigated. This development seems to differ essentially when the mixture is fired in an open tube from what it is when the tube in which the mixture is exploded is closed at the ends. In the former case it would appear, from Mallard and Le Chatelier's photographs, that the explosive wave starts suddenly during the period of vibrations; in the latter the observations of Berthelot and Dixon, and one photograph obtained by Mallard and Le Chatelier, point to the conclusion that the velocity increases continuously from the beginning until the limiting velocity of the explosive wave is reached.

The mechanism of this period of development may be represented as follows: Taking the mixture H_2+O as an example, we know from the experiments of Bunsen, Berthelot, and of Mallard and Le Chatelier, that the combustion of this mixture operated without loss of heat in a closed vessel would multiply the pressure of the mixture about nine times. Consider, then, in an explosive tube a layer of gas which has been ignited by conduction of heat; it is to a great extent free to expand, and if the combustion be slow it may happen that the pressure never exceeds considerably the initial pressure of the mixture, in which case the flame will continue to be propagated with a slow uniform velocity, or the combustion in the layer may proceed rapidly and the circumstances be less favourable to expansion, in which case the pressure of the mixture may be considerably increased, say from P to αP, where $\alpha > 1$. Now, during the process by which the next layer is fired by conduction the pressure of that layer will be increased above its original amount by the expansion of the first layer. This compression will raise the temperature of the second layer and so diminish the amount of heat required to be received from conduc-

tion in order to ignite it, and the maximum pressure reached during the combustion of this layer will be higher than aP, being nearly equal to a^2P. In this way we see that the velocity of the flame will go on increasing simultaneously with the maximum pressure reached in the combustion, until this pressure becomes sufficient to bring about ignition by adiabatic compression, when the flame will continue to move with the uniform velocity characteristic of the pressure wave.

The compression which this theory of the explosive wave compels us to assume as existing in that wave, depends on the temperature of ignition, and the ratio of the two specific heats for the mixture in question. For H_2+O we have $T=555°$, and $\gamma=1{\cdot}4$, so that a compression of over 30 is required. This assumes that T is independent of the pressure; but that is not the case, as is shown by my experiments on the ignition of explosive gaseous mixtures, described in another paper. The influence of pressure on the igniting point of H_2+O has not been examined; but it is probable that increase of pressure will be found to lower the temperature of ignition of that mixture, so that a smaller compression than 30 might suffice.*

During the development of the explosive wave, the brightness of the flame increases considerably, as is well seen in photographs of the flame of an explosion in a long glass tube, closed at each end, the mixture being fired by a spark at one end. At the same time the duration of the flame decreases considerably, according to Mallard and Le Chatelier, from several hundredths of a second, for the flame of slow uniform propagation, to less than $\frac{1}{1000}$ sec. for the explosive wave.†

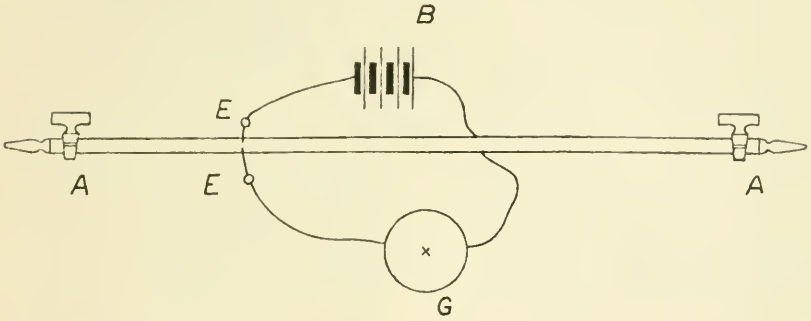
The duration of the flame is very closely connected with the duration of chemical action in the explosion (*see* Introduction), and observations of this kind would, if practicable, be the most satisfactory way of investigating the question; but, unfortunately, there are few flames bright enough to be capable of being photographed on a moving plate, at any rate during the period of

* *Vide* Mitscherlich (*Ber.* 26, 399), also Freyer and V. Meyer (*Zeit. Physikal. Chem.*, 11, 28). The question is still unsettled.—H. B. D.

† The light from the explosion wave in H_2+O remained bright enough to affect a sensitive plate less than one five-thousandth of a second.—Dixon (*Phil. Trans.*, 1893, p. 150).

development of the explosive wave. The ingenious arrangement employed by Carin and Lucas (*Ann. de Chim. et de Phys.* [4] xxvi, 477) to measure the duration of the electric spark might be applied with success; but the apparatus required would be expensive, and the observations insufferably tedious.

From what has been said in the Introduction, it will be seen that the duration of chemical action at any point in the explosion tube might be determined by measuring the time during which the gases there will conduct electricity. This it seemed possible to do by the method now to be described, which, when first devised and applied, was seen to give values of a time t and a resistance R connected with the explosive wave; but the real meaning of this time t was only perceived much later.



Method I.—The tube A A is filled with the explosive mixture, which is fired by a spark at one end. The flame of the explosion makes instantaneous contact between the two insulated electrodes E E, and allows a quantity of electricity Q to flow through the galvanometer G.

If E denote the E.M.F. of the battery B, R the resistance of the circuit supposed to be constant, we have for the equation to the current—

$$E = Ri + L\frac{di}{dt}$$

$$i = \frac{E}{R}\left(1 - e^{-tR/L}\right)$$

$\therefore \int_o^t i\,dt$ measured

$$= \frac{ET}{R} + \frac{E}{R}\left[\frac{L}{R}e^{-TR/L} - \frac{L}{R}\right]$$

$$= \frac{ET}{R} - \frac{EL}{R^2}\left(1 - e^{-TR/L}\right)$$

If $\frac{RT}{L}$ is small, we have

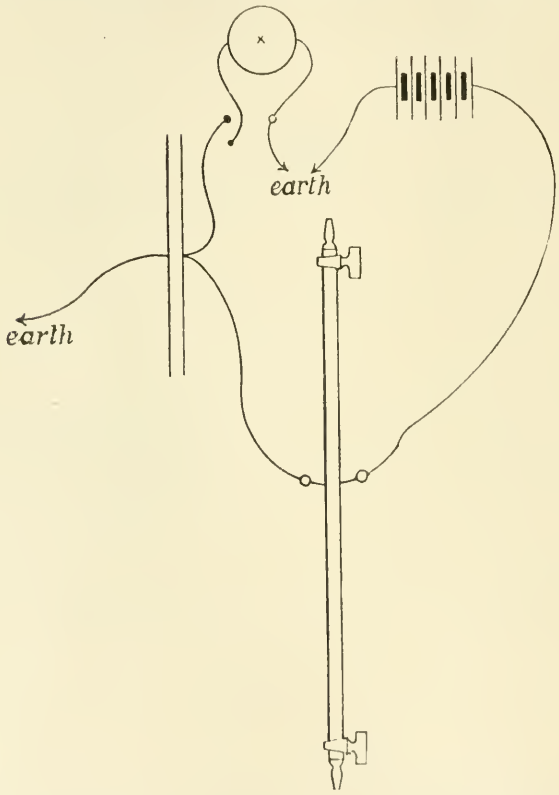
$$e^{-TR/L} = 1 - \frac{TR}{L} + \frac{T^2R^2}{2L^2}$$

$$1 - e^{-TR/L} = \frac{TR}{L} - \frac{T^2R^2}{2L^2}$$

$$\frac{EL}{R^2}\left(1 - e^{-TR/L}\right) = \frac{ET}{R} - \frac{ET^2}{2L}$$

$$\therefore \int_0^T i\,dt = \frac{ET^2}{2L}$$

This shows that the quantity of electricity flowing through the galvanometer is very small, since T is small and L large. Experiment showed the kick of the galvanometer needle observed to be very small, and the method was modified as follows :—



Method II.—The flame of the explosion making momentary contact between the insulated electrodes allows a quantity Q of

electricity to enter the condenser, which is afterwards measured by discharging the condenser through the galvanometer.

We have

$$Q = EC\left(1 - e^{-t/RC}\right)$$

$$\therefore \frac{t}{R} = -C \log_e\left(1 - \frac{Q}{EC}\right)$$

or if $\frac{t}{RC}$ be small

$$\frac{t}{R} = \frac{Q}{E}$$

By repeating the experiment with an additional resistance S introduced into the circuit, we obtain another equation :—

$$\frac{t}{R+S} = \frac{Q_1}{E'}$$

and from these two equations values of t and R can be obtained. This assumes that R remains constant during the time t, which is not true, but we may expect to obtain a value of R, which is about the mean of its instantaneous values during that time.

Apparatus.—The explosion tube first used was half-inch brass tubing; the electrodes were brass binding screws tipped with platinum, the tips being about 3 mms. in area and 8 mms. apart; the screws were insulated from the tube by means of ebonite.

Experiments.—Series I.—Seven Leclanchés used, e.m.f. = 10·2 volts. Capacity of condenser, 1·98 microfarad.

The following deflections were observed with the mixture H_2+O :—

Through R.....	273, 272, 273, 296, 291.	Mean, 281.
,, R+2000 ohms.	140, 143, 140.	Mean, 141.

It was found that a deflection of one division represented $\cdot 0181 \times 10^{-6}$ coulomb.

Whence

$$R = 1750 \text{ ohms.}$$
$$t = \cdot 0010 \text{ second.}$$

Series II.—H_2+O. Seven Leclanchés. 1·98 m.f. condenser.

Deflections :—

R.....	298, 320, 303.	Mean, 307.
R+1000.....	213, 204, 209.	Mean, 209.
R+2000.....	149, 149.	Mean, 149.

Whence

$$\frac{t}{R} = \cdot 638 \times 10^{-6} \quad \ldots\ldots\ldots \text{(i)}$$

$$\frac{t}{R+1000} = \cdot 410 \times 10^{-6} \quad \ldots\ldots\ldots \text{(ii)}$$

$$\frac{t}{R+2000} = \cdot 284 \times 10^{-6} \quad \ldots\ldots\ldots \text{(iii)}$$

From (i) and (ii) .....R=1800 ohms.
(i) and (iii).....R=1600 ohms. } Mean, R=1600 ohms
(ii) and (iii).....R=1250 ohms.

Taking as a mean value R=1600,

we have (i).....t=·00102
(ii) ..... ·00107 } Mean, t=·00104 sec.
(iii) ..... ·00102

These two series of experiments give results which are not entirely satisfactory, but still give reasonable grounds for hoping to obtain approximate measures of R and t.

Series III.—Distance between tips of electrodes, 6 mms. H_2+O Four Leclanchés used.

Deflections:—

R..... 303, 289, 230. Mean, 274.
R+2000..... 138, 133, 125. Mean, 132.

Whence R=1400 ohms.
t=·0015 second.

These results are less satisfactory, and others were obtained which were still less so; accordingly a new apparatus was made with the electrodes tipped with platinum (in the first apparatus this was not the case).

Series IV.—Platinum-tipped electrodes, tips 9 mms. apart. H_2+O. Four Leclanchés.

Deflections:—

R..... 90, 95, 99, 106, 103, 75, 72, 89, 117. Mean, 94.
R+1574..... 49, 58, 59, 66, 62, 59, 68. Mean, 60·1.

Whence R=2600 ohms.
t=·00080 second.

These results are still not satisfactory; the deflections observed vary considerably. However, the value of t is not very much different from the value in Series I and II. The apparatus had to be replaced by a modified form, as the first gave way after a number of explosions. In the new form the flame at the electrodes is almost entirely surrounded by a mass of gun metal, while in the older one it was mainly surrounded by ebonite.

Series V.—New Apparatus. H_2+O. Four Daniells.

Deflections:—

R..... .. 55, 47, 45, 48, 57, 52, 43, 55, 51. Mean, 50·3.
R+1574..... 22, 24, 27, 35, 40, 34, 32, 30, 33. Mean, 30·7.

Whence R = 2350 ohms.
t = ·00053 second.

Some experiments were then made with mixtures of H_2+O and air; the addition of one-third of the volume of air was found to reduce the deflections considerably. Subsequent experiments, however, with the mixture H_2+O itself gave deflections smaller than those at first observed. The next series of experiments given refers to the three mixtures H_2+O, H_3+O, H_4+O. Five sets of experiments were done in the order H_3+O, H_4+O, H_2+O, H_4+O, H_3+O.

Series VI.

H_3+O. R..... 17, 22, 24, 16, 23, 17. Mean, 19·8.
R+1574..... 13, 16, 13, 11, 12, 14. Mean, 13·2.
Whence R = 3100 ohms.
t = ·00026 second.

H_4+O. R ..... 13, 11, 14, 10. Mean, 12.
R+1574 ..... 7, 7, 8, 8. Mean, 7·5.
Whence R = 2600 ohms.
t = ·00013 second.

H_2+O. R..... 35, 30, 37, 43, 32, 39, 34. Mean, 35·7.
R+1574... 25, 28, 16, 18, 22, 21, 20. Mean, 21·4.
Whence R = 2150 ohms.
t = ·00037 second.

H_4+O. R..... 12, 13, 16, 13, 15. Mean, 13·8.
R+1574..... 5, 6, 8, 10, 9. Mean, 7·6.
Whence R = 1930 ohms.
t = ·00011 second.

H_3+O. R.... ..... 18, 20, 21, 20, 22, 21. Mean, 20·3.
R+1574..... 13, 12, 13, 12, 12, 14. Mean, 12·7.
Whence R = 2620 ohms.
t = ·00022 second.

The numbers obtained agree only moderately, but other experiments with various mixtures gave results which rather became less satisfactory than improved. Another form of apparatus was tried, in which the thick platinum wires forming the electrodes were fused into a strong piece of glass tubing. It was found necessary to heat the glass tube in an air bath to 103°, in order to prevent the deposition of a conducting film of moisture;

but even then the results obtained were not satisfactory, and became less so as the apparatus became older. Finally, the glass tube was smashed by an explosion, and the experiments were abandoned.

The results obtained by these experiments, which were very tedious and required a great amount of time, are somewhat small. I think we may conclude from them that the mean resistance of the flame of an explosion of H_2+O, taken between electrodes such as were used, is between 1500 and 3000 ohms, and that the time during which the flame conducts is not very much different from ·001 of a second.

The resistance obtained is very small for that of a flame, far smaller than has yet been observed with steady flames; this is accounted for by the facts that the flame of the explosive wave in H_2+O is hotter than the flame of the oxyhydrogen blowpipe, and that in this flame the pressure is, during part at least of the time, very high. That the flame of the explosive wave is hotter than that of the oxyhydrogen blowpipe follows from the high pressure reigning in it, since increase of pressure reduces dissociation; and from the further consideration that in the explosive wave each layer of gas is raised suddenly to a temperature considerably above its minimum igniting point (otherwise the combination would not be completed in ·001 second), while in the oxyhydrogen flame the mixture of gases is raised to a temperature which is barely sufficient to ignite it. Moreover, in the oxyhydrogen flame, the gases are free to expand, and the specific heat at constant pressure is the effective one; while in the explosive wave there is not time for complete expansion, and, indeed, the specific heat at constant volume appears to be the one which comes into play.

As to the value of t, although the experiments do little more than give the order of magnitude, they still have some importance in connection with the hypotheses which have been advanced concerning the velocity of the explosive wave. Berthelot's formula equates this velocity to the mean velocity of translation of the molecules at the moment of combination, on the supposition that they retain all the heat developed by the chemical change; Dixon, on the other hand, approximates the velocity of explosion to the velocity of a sound-wave in a mixture of burning and burnt gases

heated to the temperature which prevails in the wave-front, and this temperature is calculated to be twice that due to the chemical reaction alone.

Of the two formulæ Dixon's appears to be the more correct theoretically, and the experimental results agree well with it in most cases, but there are some considerable deviations. Now, if t, the duration of chemical action, be of the order of ·001 second, then it follows from the known velocity of the explosive wave that the front will have advanced something like 2 metres before the chemical action is complete, and it seems impossible that the velocity of the wave should be determined by the *total* amount of heat set free in the reaction, Q, when some of this is developed only after the front of the wave has advanced a metre or more. It is plain that some fraction only of Q is effective, and the smaller t is the larger will be this fraction, so that we may expect considerable differences between the theoretical and experimental rates of explosion in the case of mixtures where t is found to be large, while a closer approximation between the two values should be observed when t is small. This is borne out by the following numbers:—

Σ = velocity calculated by Dixon's formula.

v = observed velocity.

	H_2+O	H_4+O
Σ	3416	3585
v	2821	3268
t	·00024	·00012

and if some more convenient method for obtaining the value of t could be utilised it would in all probability be found that large differences between Σ and v occur in those cases for which t is comparatively large, or, in other words, when there is considerable dissociation in the wave-front.

The measurements of t, as far as they go, confirm the hypothesis put forward by Dixon: that in the explosion of the mixture H_2+O there is considerable dissociation in the wave-front, but that as one or other of the ingredients of the mixture is added in excess the dissociation diminishes.

INCOMPLETENESS OF COMBUSTION IN GASEOUS EXPLOSIONS.

By Harold B. Dixon, F.R.S. (*Professor of Chemistry*), *and* H. W. Smith, B.Sc. (*Dalton Chemical Scholar in the Owens College*).

(From the Memoirs of the Manch. Lit. and Phil. Society.)

IN the course of an investigation, in which we were engaged on the rate of propagation of gaseous explosions, it was noticed that when a mixture of hydrogen and oxygen, in the proportions in which they combine to form water, was exploded, there remained an explosive residue in addition to the unavoidable slight excess of one or the other gas due to inaccuracy in mixing. The mixture was exploded in a leaden tube 100 metres long and 9 mms. in diameter; after the explosion the tap at the end furthest from the point of ignition was opened, and air allowed to rush in. Air was then pumped in by a bellows, and the other tap was then opened. On applying a light to the outrushing gases, for the purpose of determining whether the hydrogen or the oxygen was in excess in the original mixture, the gas at first driven out proved to be rich in oxygen—supporting combustion vividly—and then the succeeding gas burnt with a series of sharp cracklings, and finally there was a flash down the tube.

From this, it appeared that even in a mixture of hydrogen and oxygen, containing a slight excess of oxygen, the hydrogen was not completely burnt. If the mixture had contained an excess of hydrogen it might have been reasonably supposed that the explosive residue was made up of the excess of hydrogen and the air admitted after the explosion. This explanation could not be

admitted in the present instance, as the mixture contained an excess of oxygen. A similiar phenomenon was observed when a slight excess of hydrogen was employed, and the residue was swept out of the tube by a stream of carbonic acid gas.

Led by these experiments we began the investigation, an account of which is given in the following paper. Our object was to determine the conditions affecting the amount of this explosive residue—especially the influence of the surface exposed to the exploding gases.

Mixtures containing slight excess, first of hydrogen, and then of oxygen, were employed, and in all cases the residues were collected and analysed. The first series of experiments was made with the tube mentioned above, which was 100 metres long and 9 mms. in diameter, the surface exposed to the gases being about 29,000 sq. cms. After each explosion CO_2 was admitted at one end of the tube until the pressure was equal to that of the atmosphere, and then 1 litre was driven out and collected over caustic soda solution at the other end of the tube. It was found that the first litre driven out contained practically all the gas left after explosion. The amount of residue varied from 100 to 250 c.c., according to the accuracy of the mixture and the amount of nitrogen as impurity in the original gas, and of air in the CO_2. We give below the mean results of analysis of a considerable number of residues; those given under A resulting from a mixture containing an excess of hydrogen, whilst in those given under B and C, the original gas contained oxygen in excess.

I.

Explosions of Hydrogen and Oxygen.

(Capacity of tube, 8,100 c.c.; diam. 9 mms.; internal surface 29,000 sq. cms.).

Mean composition of residue:—

	A.	B.	C.
H_2	51·3	29·5	20·5
CO		5·1	5·8
O_2.....	19·4	38·1	32·7
N_2.....	26·3	27·3	41·0
	100·0	100·0	100·0

Percentage of original detonating gas unburnt:—

	A.	B.	C.
Maximum	1·08	·92	1·07
Minimum	·69		
Mean	·88		

With regard to the calculation of the amount of unburnt detonating gas, a slightly different method is employed, according as the original gas contains excess of oxygen or hydrogen. All the residues contain a certain percentage of nitrogen, part of which is due to inleakage of air, and to air in the CO_2, used for sweeping out the tube, whilst part exists as impurity in the original gas, being chiefly derived from the water in the gas-holder. It is, however, impossible to determine accurately how much is due to each cause. In calculating the percentage of unburnt detonating gas, a maximum and minimum are taken in the following way. Firstly, assume all the nitrogen was present in the original gas, and calculate all the oxygen as belonging to the unburnt residue. This gives a maximum value for the percentage unburnt. Secondly, assume that all the nitrogen got in (as air) after the explosion, and from the percentage of oxygen, deduct the amount of oxygen corresponding to the nitrogen (as air). In this way we get a minimum value for the amount of unburnt detonating gas, and the true percentage must lie between these limits. If there is a sufficient excess of oxygen, we get only one value for the unburnt residue, viz., $1\frac{1}{2}$ times the residual hydrogen. It will be observed that each of the residues contains a small percentage of carbonic oxide. Part of this is probably due to the grease used for the taps, and part may be due to hydrocarbons derived from the zinc used in the preparation of the hydrogen (except in cases where electrolytic gas was used). The carbonic oxide, being a combustible gas, must be taken into account in calculating the residual detonating gas. When there is an excess of oxygen, the carbonic oxide is liable to get burnt, and therefore should be considered as a portion of the detonating gas left unburnt. When there is a deficiency of oxygen, the carbonic oxide may be classed with the excess of hydrogen left over, and whether it affects the amount of unburnt detonating gas depends upon the quantity of oxygen remaining.

To determine the influence of the amount of surface exposed to the gases, a tube 4 mms. in diameter was next employed. The length was about 170 metres, and the internal surface 25,000 sq. cms., the capacity being 2,750 c.c. The method of procedure was the same as before. Under A, in the following table, is given the mean of several analyses of residues from mixtures containing an excess of hydrogen, and under B, the mean result from mixtures containing an excess of oxygen.

II.

	A.	B.
H_2	46·1	38·6
CO	14·9	12·4
O_2	16·3	25·4
N_2	22·7	23·6
	100·0	100·0
Average residue	75 c.c.	82 c.c.
Percentage of original detonating gas unburnt :—		
Maximum	1·34	2·27
Minimum	·84	1·55
Mean	1·09	1·91

The percentage unburnt, under A, does not differ much from that obtained with the wider tube. Under B we see a rather larger percentage. In the next tables are given the means of analyses of residues obtained with a tube 19 mms. in diameter (III),* and lastly (IV),† with an iron bomb made out of an ordinary mercury bottle attached to a firing tube. In the latter, there are only about 1,600 sq. cms. of surface exposed for a volume of 3,075 c.c.; that is to say, a surface only one-fifteenth as great as that exposed in the 4 mm. tube, the capacities being, however, nearly equal. From the analyses it would appear that although the amount of surface exposed to the gases has some influence on the amount unburnt, the influence is not very great, and therefore it seems improbable that the incompleteness of combustion is due primarily to the cooling action of the surface of the vessel.

* Four experiments were made with the same mixture.

† Seven experiments were made with the same mixture.

III.		IV.
C = 14,000 c.c.		C = 3,075 c.c.
d = 19 mms.		d = 100 mms.
S = 28,000 sq. cms.		S = 1,600 sq. cms.
Average residue 235 c.c.		100 c.c.
Mean composition of residue :—		
H_2	44·2	8·2
CO	18·0	1·2
O_2	22·7	31·1
N_2	15·1	59·5
	100·0	100·0
Percentage. of detonating gas unburnt :—		
Maximum .....1·16		·46
Minimum ..... ·86		
	1·01	

A number of experiments were made with a mixture of carbonic oxide and oxygen.

In the first series of experiments the 9 mm. tube was employed, and in the second series the iron bomb. The mean results are given below.

Carbonic Oxide and Oxygen.

I.		II.
C = 8,100 c.c.		C = 3,075
d = 9 mms.		d = 100 mms.
S = 29,000 sq. cms.		S = 1,600 sq. cms.
Average residue 205 c.c.		55 c.c.
Mean composition of residue :—		
CO	26·0	41·4
H_2	1·7	6·7
O_2	30·2	27·1
N_2	42·1	24·8
	100·0	100·0
Percentage unburnt :—		
1·06	Maximum 1·17	
	Minimum 1·01	
	Mean 1·09	

In this case, therefore, we have also about 1 per cent. of the original detonating gas left unburnt. The surface here does not appear to have much influence, the percentages unburnt being almost the same, although the surface exposed to the gases was, with the tube, about $3\frac{1}{2}$ sq. cms. for each 1 c.c. of gas burnt, against ·5 sq. cm. per 1 c.c. of gas burnt with the bomb.

The fact that the incompleteness of combustion is characteristic of the explosive wave, and is not observed in the ordinary combustion in a eudiometer, has an important bearing on the theory proposed by Berthelot, to explain the mode of propagation of the explosive wave, and also seems to confirm the observation made by Mallard and Le Chatelier, that the rate of cooling in this method of combustion is much more rapid than in the ordinary combustion.

ON THE COMBINATION OF HYDROGEN AND CHLORINE, ALONE, AND IN PRESENCE OF OTHER GASES.

By Harold B. Dixon, M.A., F.R.S. (*Professor of Chemistry*), *and* J. A. Harker (*Research-Student in the Owens College*).

(From the Memoirs of the Manch. Lit. and Phil. Society.)

Is the combination of hydrogen and chlorine affected by the presence or absence of moisture? Does hydrogen, when exploded with an excess both of chlorine and of oxygen, unite entirely with the chlorine or divide itself between the two?

The evidence on the first point is conflicting; on the second we have the definite statement of C. Bötsch (*Annalen* ccx, p. 207) that the hydrogen does not divide itself between the chlorine and oxygen, but goes entirely to the chlorine. Bötsch's experiments, however, are not accurate enough to make us feel sure of his conclusion, which he admits is *à priori* improbable.

In a communication made to the Chemical Section of the British Association at Newcastle in 1889 we brought forward some evidence bearing on these questions. Our object was to work out the law according to which hydrogen divides itself between chlorine and oxygen in an explosion of the three gases. It was first necessary to determine whether direct union between dry hydrogen and chlorine takes place under the conditions of our experiments. We found that sparks from an induction coil, passed through the gases between wires of platinum-iridium, caused the instantaneous explosion of the mixture after it had been standing for days in contact with anhydrous phosphoric acid. Combination between dry hydrogen and chlorine is

therefore determined by the spark, just as combination between dry hydrogen and oxygen is determined by the spark.

On the other hand, the action of light on a mixture of hydrogen and chlorine is affected by the presence of moisture. In the course of our experiments on hydrogen and chlorine (which were begun in 1882) we have on several occasions noticed the difficulty of exploding dry hydrogen and chlorine by a flash of light. The same observation has been made by other chemists, of whom we may mention Mr. W. A. Shenstone. But the fact was not, so far as we know, published until 1887, when Pringsheim,* in his admirable paper on the chemical action of light on hydrogen and chlorine, stated that the mixture when long dried by phosphoric acid exploded only after a few seconds in sunlight and with a weak clicking sound; and that in diffused daylight the formation of hydrogen chloride was greatly retarded.

In order to compare the action of light on the wet and dry mixture of hydrogen and chlorine, we filled a row of six bulbs with the electrolytic gas, and sealed them up. In the last two bulbs sticks of anhydrous phosphoric acid were placed, so that the gases were sealed up in contact with the drying agent. After lying in the dark some weeks, a wet and dry bulb, screened one from the other, were exposed to the light of a magnesium "flash" placed 6 feet from the two. Neither exploded; but on firing a similar flash 5 feet from the two, the wet bulb exploded loudly, the dry bulb was unaffected. On firing flashes at 4 and 3 feet from the dry bulb, no action was observed. Fired at 2 feet from the dry bulb, the flash produced a loud explosion. In other experiments similar results were obtained. When the electrolytic gas was well dried before admission to the bulb, and was then sealed up with phosphoric acid, and kept several weeks, it could not be exploded by the flash at 1½ feet. We may state, as a general result, that a magnesium flash (which will invariably explode a wet mixture of hydrogen and chlorine at 5 feet distance) has to be brought within 1 foot in order to explode a well-dried mixture of the same gases; in other words, the intensity of the light must be increased 25 times to produce the same effect on the dry as on the moist gases. This difference in the

* *Annalen der Physik*, 1887. N F., xxxii, p. 421

action of light is so well marked that we have continually made use of it as a test of the dryness of the electrolytic gas used in our experiments on the volume-relation of hydrogen and chlorine to the hydrogen chloride gas formed from them.

To determine the law which regulates the division of hydrogen between chlorine and oxygen, in an explosion of the mixed gases, it is essential that the gases should be accurately measured. All our attempts to measure chlorine in a eudiometer over a liquid have failed. Oil of vitriol (used by Bötsch) absorbs chlorine; liquid chlorinated hydrocarbons absorb chlorine rapidly. We have had to measure chlorine by filling a glass explosion vessel of known capacity with it under known conditions; and have then introduced into the same vessel known volumes of hydrogen and oxygen. Our latest apparatus consists of two strong bulbs (of 180 c.c. and 140 c.c. capacity), which can be put into communication through a wide tap. Each bulb can be filled separately; for instance, one may be filled with electrolytic hydrogen and chlorine, and the second with oxygen, or one may be filled with electrolytic hydrogen and oxygen, and the second with chlorine. The two bulbs are then put into communication, and the gases allowed to mix by diffusion. A pressure tube is attached to the bulbs, and is shut off by a stop-cock. This tube is filled with an inert gas, *e.g.*, nitrogen, and dips into a mercury trough. When all is ready for an explosion the tap of the pressure tube is opened for a moment and then closed. The height of the mercury in the tube gives the pressure in the bulbs. By having the gases in the bulbs slightly below the atmospheric pressure a little nitrogen from the pressure tube enters the bulb, and no chlorine escapes into the pressure tube. After firing at a suitable temperature, the temperature can be reduced to the same point as before. Then on opening the tap of the pressure tube the rise of mercury indicates the diminution in volume of the exploded gases. If hydrogen and chlorine united without contraction to form an equal volume of hydrogen chloride gas, and if the hydrogen united entirely with the chlorine and not with the oxygen at all, then no alteration in volume would result from the explosion.

However, on firing the well-dried mixture of the three gases by a spark at ordinary temperatures, a *cloud* is formed, and a considerable *contraction* is shown by the pressure tube. We have found a contraction of over 10 per cent. of the original volume of

gases—*due partly to the formation and condensation of steam, and partly to the formation of hydrogen chloride and to its solution in the water condensed.* We say that the condensation is partly due to the formation of hydrogen chloride, because we have found that however carefully the bulbs and the gases are dried, there is a sensible contraction when hydrogen and chlorine combine in a glass vessel. This contraction is rather over 1 per cent. of the original volume. We have varied the apparatus and the manner of working, but we always find nearly the same result—whether the gases are exploded or whether they combine gradually in diffused light.

The fact that the hydrogen *divides* itself between the chlorine and the oxygen is proved by the large contraction, by the cloud, and by the visible drops which condense on the surface of the bulb.

Proof of another kind is afforded by the fact we have established, that chlorine is liberated when hydrochloric acid is mixed with equal volumes of hydrogen and oxygen and the mixture is exploded. The excess of heated oxygen takes hydrogen from the hydrogen chloride under these conditions, which are comparable with those obtaining when a mixture of hydrogen, chlorine, and oxygen is exploded.

Since our communication was made at the Newcastle meeting, and after a brief account of it had appeared in *Nature* (October 10), a paper was published in the *Comptes Rendus* (October 21) by MM. Hautefeuille and Margottet—"Sur la synthèse simultanée de l'eau et de l'acide chlorhydrique." These authors find that hydrogen divides itself between chlorine and oxygen, unless the volume of chlorine is relatively large. When the chlorine is in large excess *only* hydrochloric acid is formed. The experiments appear to have been made at ordinary temperatures.

THE RATE OF EXPLOSION OF HYDROGEN AND CHLORINE IN THE DRY AND IN THE MOIST STATES.

By Harold B. Dixon, M.A., F.R.S. (*Professor of Chemistry*), *and* J. A. Harker (*Dalton Chemical Scholar in the Owens College*).

(From the Memoirs of the Manch. Lit. and Phil. Society.)

THIS research, a continuation of our previous work on the combination of chlorine and hydrogen, was made with the object of ascertaining whether, in the explosive combination of these gases, the action was a direct one, or whether the union was brought about by the interaction of water-vapour present. We have already shown (confirming Pringsheim's statement) that the gases, when thoroughly dried, were not nearly so sensitive to light as when in the moist condition, about 25 times more light being necessary to explode the dry gas than that saturated with moisture. The question remained: When once the explosion is started in a portion of the mixed gases (either by light or by a spark), is the propagation of the explosion through the unburnt gases dependent on the presence of water-vapour? The method employed to solve this problem was the same as that previously used to determine whether the combustion of carbonic oxide and of cyanogen by oxygen was effected by the interaction of water-vapour. In the case of carbonic oxide and oxygen the rate of propagation of the combustion is increased by adding water-vapour until it amounts to about 5 per cent. of the mixture; in the case of cyanogen and oxygen the rate of propagation of the

combustion is diminished by the addition of water-vapour to the dry gases. The burning of cyanogen, at all events as far as the initial combustion to carbonic oxide is concerned, seems to be independent of the presence of water; whereas the combustion of carbonic oxide to carbonic acid seems to depend upon the presence of water-vapour. A measurement of the rate of explosion of hydrogen and chlorine, firstly in the dry state, and, secondly, when saturated with water-vapour, seemed, therefore, likely to answer the question.

A knowledge of the velocity of the explosion-wave in hydrogen and chlorine is also of great theoretical interest in view of Berthelot's conclusions regarding the nature of explosions: for hydrogen and chlorine combine without condensation, and the gas formed approximates to a perfect gas.

The gas used in the experiments was made by the method so minutely studied by Bunsen and Roscoe, viz., the electrolysis of hydrochloric acid. The acid used (of specific gravity about 1·20) was partly saturated with chlorine gas, to save the long preliminary electrolytic saturation otherwise necessary. The electrolytic cell was of glass, and contained about 3 litres of acid. It was provided with two carbon electrodes, about 10 mms. thick, cemented by paraffin into glass tubes, which dipped below the level of the liquid. The upper ends of these tubes were filled with mercury, making contacts for the battery wires. The delivery tube contained a series of bulbs holding about 5 c.c. of water. This retained the greater part of the hydrochloric acid carried over by the chlorine and hydrogen. From this the gas was conducted through a Winckler worm, a series of bulbs, and finally a large U tube, all filled with *boiled* sulphuric acid. Attached to the U tube was a three-way tap, one limb of which led to the explosion tube, and the other to a tower filled with lime and charcoal. The whole apparatus was mounted on a stand, and the glass tubes were fused together after filling. The current used was supplied from seven large secondary cells, giving a voltage of about 15. It passed through two adjustable resistances; one, iron wire, the other, carbon; then through a small low-resistance Kohlrausch ammeter; then to the electrolyser. About 4 ampères was the greatest current we could use without heating the liquid too much.

We first experimented with a view to discover a material suitable for the explosion tube. Pieces of pure lead sealed up in dry chlorine are not much acted on, the colour of the gas being visible after some weeks. We, therefore, thought that a lead tube, after a certain time, would become coated internally with chloride, and so be available at least for the experiments with dry gases. After many hours of saturation with dry chlorine, we found that the gas continued to be absorbed with formation of a white volatile solid decomposed by water, which analysis showed to be chloride of tin. This issued as a white cloud from the end of the explosion tube. The best electrolytic mixture we could obtain from the end of the explosion tube contained not more than 80 % combustible gas ($H_2 + Cl_2$).

We, therefore, proceeded to have drawn some strong glass tubing in long lengths. We succeeded in getting two lengths of 30 and 34 feet respectively. These were slung from a long ladder fixed against the wall of a dark corridor. One end of each tube was then bent and fastened to the other, so that the whole tube was about 21 yards long. Various joints were used, plaster of Paris, certain cements, and also fused chloride of silver, but none of these held so well as a piece of strong rubber, slipped over the ends, which were previously ground smooth and pressed close together. The rubber, being coated on the inside with paraffin, was acted on very slowly by the chlorine. Fastened to the two free ends of the tubes were steel flanges with ground faces. Their interior was lined with glass.

The gas passed directly from the electrolytic cell through the drying tubes into the long explosion tube — driving out the air before it; at the further end it passed through an "analyser," which served to determine the composition of the gas issuing from the tube. This consisted of a large bulb holding 80 c.c., provided at the bottom with a three-branch tap leading to a funnel containing dilute KI solution and to a small bottle containing water. At the upper end was a tail-tap leading to a pipette and to a lime and coke tower. The pipette, which was constructed of narrow tubing about 6 mms. diameter, was provided with a millimetre scale and calibrated by mercury. The tube between the three-way tap and the pipette was very fine, less than 1 mm. bore. The dry gas was passed from the explosion tube through

water into the bulb, which had been previously dried; then the excess passed into the tower. After collecting the sample the taps were all closed, the gas pipette being completely full of water.

The bulb was first exposed for some time to diffused daylight and then to sunlight or to some magnesium flashes. The tap below was then opened to the KI reservoir, and the liquid allowed to rush up. A small residue generally remained, which was measured in the pipette. This small residue was found to be hydrogen; it was never more than 1 per cent. of the whole, and in most of the experiments varied between ·2 and ·4 per cent.

To insure complete combination between the hydrogen and chlorine in the bulb by the action of light, it was necessary to moisten the gases. The gases as used in the dry experiments may be exposed for days to sunlight without complete combination taking place. The potassium iodide serves to show that there is no chlorine left.

The filling of the explosion tube took generally two to three hours with the average current. The whole of the generating and drying apparatus was protected from light by being covered with black cloth, and the corridor was only illuminated by one or two small gas flames, which did not have the least perceptible action on the mixture.

The method used to measure the rate of the explosion wave was similar to that used for other gaseous mixtures, viz., to make the explosion break two silver or platinum strips or "bridges" stretched across the tube, one near each end. These bridges carried currents, which actuated two electro-magnetic styles making traces on a moving plate. The bridges were fitted to two separate tubes, which could be rapidly joined up to the long glass explosion tube by means of steel flanges. These separate "end tubes" were charged with a mixture of oxygen and hydrogen. When the long tube was completely filled with the electrolytic hydrogen and chlorine, the two "end tubes" carrying the bridges were fastened to it, the electric connections were made to the chronograph, and the gases fired by sending a spark through the oxygen and hydrogen in the firing tube. The flame travelled down this tube, which was about 4 feet long, breaking the silver bridge at the end of it, and communicating the explosion

to the hydrogen and chlorine. On reaching the end of the glass tube, the explosion broke the silver bridge fitted to the second end-tube. In the few seconds which elapsed between joining on the end tubes and firing the mixture, but little diffusion of the gases was possible; and the silver bridges, being coated with paraffin, were hardly acted on by the chlorine. Between each experiment all the connections of the chronograph were reversed; so that whatever error was due to the defects of the chronograph and connections was reversed in the second experiment. The results are therefore grouped together in pairs, the means of the several pairs being closely concordant. The following are the results obtained in the first series of experiments:—

$$H_2 + Cl_2.$$

Rate of Explosion in Metres per Second.*

Dry.	Wet.
1776, 1821 } 1798	1728, 1786 } 1757
1791, 1799 } 1795	1740, 1809 } 1774
1764, 1811 } 1787	1787, 1772 } 1780
1728, 1869 } 1798	
1767, 1832 } 1800	
Mean..1795	Mean..1770

Difference due to water present = 25 met. per second.

It appears, therefore, that the explosion, once started, travels slightly faster in the dry gases than in the wet, the moisture appearing merely to act as a diluent.

* It was discovered afterwards that both series of measurements were affected by a small constant error which made the results too high.

EXPERIMENTS ON THE TRANSMISSION OF EXPLOSIONS ACROSS AIR GAPS.

By Bevan Lean, B.Sc. (*Dalton Chemical Scholar*), *and* Harold B. Dixon, F.R.S. (*Professor of Chemistry in the Owens College*).

(From the Memoirs of the Manchester Lit. and Phil. Society.)

HOW far the shock produced by the explosion of a gaseous mixture can be transmitted through a column of air so as to ignite a gaseous mixture beyond, is a question often asked in the discussions raised as to the nature of colliery explosions. Some practical men have expressed the opinion that the shock can be transmitted through air along great lengths of straight gallery, so as to cause the explosion of accumulations of fire-damp at the further end; others hold that a few score yards of gallery free from fire-damp and dust will effectually prevent the propagation of an explosion in a mine. To obtain some data by which to decide the question, the following experiments were tried on the small scale.

Apparatus.—The apparatus consisted of two lead tubes, 880 mms. in length, and 17½ mms. internal diam., which could be connected together by glass tubes of varying dimensions by means of brass junctions.

Explosive Mixture.—The explosive mixture employed was one of two vols. of hydrogen mixed with slightly more than 1 vol. of oxygen. The mixture was kept over water in an iron gas-holder. The hydrogen was made from zinc and sulphuric acid, without special purification, and the oxygen was prepared from potassium chlorate.

FIG. 1.

A and B are two lead tubes, 880 mms. in length, and 17½ mms. internal diam.
E C is a glass firing piece, fixed to A by Faraday's cement.
L is a steel tap fixed to the firing piece by Faraday's cement.
D F is a strong glass tube fixed in between B and a steel tap by Faraday's cement.
X is a glass tube fixed to the two brass junctions by means of Faraday's cement.

The means for connecting either brass junctions up to A or B is shown in Fig. 2.

U V is a circular ring which when screwed up over W Y makes an air-tight connection between the brass piece and the lead tube A.

G and H (Fig. 1) are small brass tubes, provided with taps by means of which A may be placed in communication with B, without making use of X.

T and S are large taps in the brass junctions, connecting X with A or B. The passage in each tap is 11 mms. in diameter.

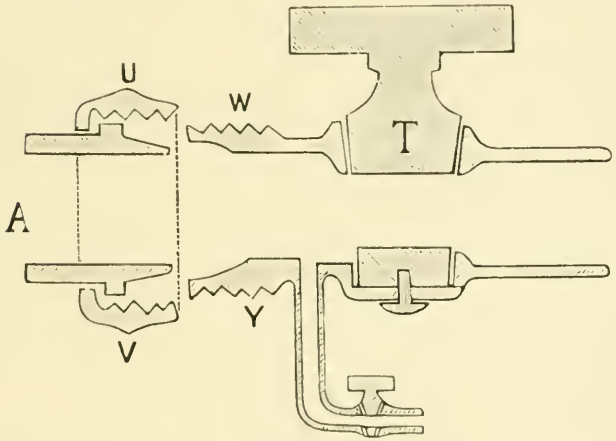


FIG. 2.

Method of Experiment.—After passing a current of air through the apparatus, air was enclosed in the tube X by turning off the taps T and S. The tube G was then connected with H by means of an india-rubber tube, and the explosive gas passed in at L, and through the apparatus, until a sample taken at F was found to explode violently. The taps at E, F, G, and H were then all turned off, and the platinum wires in the firing piece connected up with a Ruhmkorff coil. One observer then stationed himself opposite the tube X, and immediately before giving the command to fire, quickly turned on the taps T and S. A second observer, placed opposite D F, thereupon broke the primary circuit of the coil, producing a spark in E C, and at the same time closely watched D F for any flash indicating that the mixture in B had been fired across the air gap by the explosion in A.

Though the glass tube D F was very strong, it was found necessary to wrap wire gauze around it, inasmuch as it was several times shivered to pieces by the violence of the explosion wave. Though the glass tubes employed between A and B were frequently comparatively weak, experience showed that the pressure produced by the explosion against the wall of the tube X was so small, that the tube was in no case burst.

First Series of Experiments. A number of experiments were made with glass tubing of 20 mms. internal diameter, of various lengths. After fixing the glass tube by means of Faraday's cement to the two brass junctions, the distance from the centre of the tap T to the centre of the tap S was measured. Only these experiments in which this distance T S is exactly the same, are made under the same conditions: it is not sufficient to make experiments with a particular tube of say 200 mms. length at one time, and again at a subsequent period, without making sure that the tube is fixed on to the brass pieces in the same manner. Differences in the length of T S with the same glass tube to the extent of 10—15 mms. may easily occur, which subsequent experiments will show to be very important. We shall therefore class experiments according to the length of T S. The volume of the air gap was determined in each case by titration with water.

(1) TS=283 mms. Vol. of air gap 73 c.c.

The flash produced by the explosion in A traversed the whole length of X, but the mixture in B was not fired.

Six experiments made, with the same results.

(2) TS=215 mms. Vol. of air gap 53·6 c.c.

B not fired by explosion in A.

Six concordant experiments made, May 6.

On May 9 the experiment was repeated, employing the same glass tube, the same mixture of hydrogen and oxygen, T S being 215 mms., as before. In four successive experiments B was fired by the explosion in A, but in two of these the glass tube D F exploded with great violence, and in the other two the cement at one or other junction was cracked. Thus, in these four experiments, in which B was fired, the pressure in the apparatus was relieved since, therefore, it

seemed conceivable that in cases in which the limit had been nearly reached, such relief of the pressure might enable A to fire B across the air gap, it appeared advisable in future experiments only to accept as conclusive those in which every junction had stood intact the shock of the explosion.

Four more experiments were made, in which the apparatus successfully stood the explosion, and in each case B was not fired.

(3) TS = 175 mms. Vol. of air gap 38·2 c.c.
B fired by explosion in A.
Three experiments made, May 9.
Five experiments made, May 12.
Thus the desired limit is to be found when TS lies between 215 and 175 mms.

(4) TS = 205 mms. Vol. of air gap 48·5 c.c.
B not fired by explosions in A.
Two experiments made—cement intact.

(5) TS = 184 mm. Air gap = 40 c.c.
B fired. Two experiments.

(6) TS = 192 mms. Air gap = 43 c.c.
B fired. Two experiments.

(7) TS = 196 mms. Air gap = 44·7 c.c.
B not fired. Three experiments.

Thus the limit is to be found between (6) and (7).

Second Series of Experiments.—A number of experiments were next made employing much narrower tubing to enclose the air gap, viz., 8—8½ mms. internal diameter, instead of 20 mms., as in the former experiments.

(1) TS = 275 mms. Air gap 17·5 c.c. Internal diam. 8·5 mms.
B fired. Three experiments.

(2) TS = 389 mms. Air gap 27 c.c. Bore 8·5 mms.
B fired. Four experiments.

(3) TS = 532 mms. Air gap 32¼ c.c. Bore 8·5 mms.
B fired. Four experiments.

(4) TS = 588 mms. Air gap 31¼ c.c. Bore 8·0 mms.
B fired. Four experiments.

(5) TS = 665 mms. Air gap 38·2 c.c. Bore 8·0 mms.
B not fired. Three experiments.

(6) TS = 656 mms. Air gap 37·6 c.c. Bore 8·0 mms.
B fired. Two experiments.

(7) TS = 663 mms. Air gap 38·1 c.c. Bore 8·0 mms.
B not fired. Two experiments.

Thus the limit is found between (6) and (7).

We can now advantageously compare the main results of these two series of experiments.

In series (1).

If TS = 196 mms., and air gap = 44·7 c.c., B is not fired.

If TS = 192 mms., and air gap = 43·0 c.c., B is fired.

In series (2).

If TS = 663 mms., and air gap = 38·1 c.c., B is not fired.

If TS = 656 mms., and air gap = 37·6 c.c., B is fired.

It would appear, therefore, that the question as to whether B shall be fired by A through a given air gap, depends upon the volume of air interposed, rather than upon the length of the column of air.

To test this conclusion a bulb was blown upon a portion of the glass tubing (bore 8·0 mms.) used in series No. 2, and this was substituted for the ordinary glass tube between the two brass junctions.

(1) TS = 198 mms. Vol. of air gap 83·5 c.c.
B was not fired.

(2) TS = 144 mms. Vol. of air gap 78·8 c.c.
B was not fired, though the bulb was filled with flame.

The two experiments last mentioned bear out the conclusion that for a given mass of a gaseous explosive mixture, there is a certain minimum mass of air which will, if interposed between it and another explosive mixture, guard this last in the manner of a protective shield or plug, and that it is practically immaterial whether this air be enclosed as a short and broad, or a long and narrow column.

ON THE DECOMPOSITION BY SHOCK OF ENDOTHERMIC COMPOUNDS.

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IN his work "Sur la Force des Matières Explosives," published in 1883, M. Berthelot described some experiments on the decomposition by shock of certain bodies formed with absorption of heat. Most of his experiments were made on gases. He exploded a charge of 0·1 grm. of fulminate of mercury, in a strong glass tube holding about 25 c.c. of the gas. With acetylene the experiment always succeeded, only about ·01 c.c. gas remaining undecomposed, and a deposit of very finely divided amorphous carbon being left on the walls of the vessel. Cyanogen was sometimes wholly decomposed, sometimes not at all. The other gases he succeeded in breaking up were nitric oxide and arseniuretted hydrogen. The decomposition, started by the fulminate, is, according to Berthelot, a detonation propagated from layer to layer with extreme rapidity, and is of the same nature as the "explosion wave."

In the *Journal of the Chemical Society* for 1889, Prof. Thorpe stated that he had discovered accidentally that carbon bisulphide could be detonated with a bright flame in the same way, yielding a mixture of carbon and sulphur. No explosive, he says, would cause the decomposition except fulminate of mercury, and the brown powder, obtained by the action of a fluid alloy of potassium and sodium on carbon bisulphide. The explosion of one-twentieth of a gram of mercury fulminate will decompose the carbon

bisulphide vapour filling a tube 600 mms. long and 15 mms. diameter. Thorpe accepts Berthelot's explanation, which he gives as follows: "The shock of the explosion communicates to the layer of gaseous molecules in immediate proximity to the fulminate an enormous active force, whereby the 'molecular edifice' is shaken to pieces, and the initial active force is augmented to a degree corresponding to the heat evolved in the decomposition of the gas. A new shock is thereby produced in the next layer, and the action is repeated, and so propagated."

According to this view, it would seem that the explosion, once initiated in cyanogen, acetylene, or carbon bisulphide, should travel as far as the gas extends, and that the rate of explosion should conform to the laws governing the propagation of the explosion wave in gaseous mixtures. It appeared, therefore, of interest to determine whether the explosion, set up by the shock of the fulminate, was propagated along a tube filled with one of the gases; and, if so, to measure the rate at which the flame was propagated.

The first gas tried was acetylene. To produce the shock a mixture of acetylene and oxygen (2 vols. to 3), one of the most violently explosive gaseous mixtures, was fired in contact with the acetylene. A coiled leaden pipe, 13 mms. in diameter and 20 metres long, was provided with a glass firing piece and tap at one end, and, at the other, a detachable tube of strong glass and a second tap. The whole was first filled with acetylene, and then a mixture of acetylene and oxygen was driven in at the firing end, so as to form a column of about a metre in length. The taps were then closed, and the mixture fired by a spark. The explosion made the "ping" on the walls characteristic of extreme violence, but the flame did not appear at the further end of the tube. On examination it was found that the great bulk of the acetylene was undecomposed. The experiment was repeated, with the same result.

An apparatus was then fitted up, to test the action of fulminate of mercury. It consisted of a steel cylinder or "bomb," holding about 400 c.c., provided with a screw top, through which passed insulated copper wires, and having a tap for admission of gas. This was connected by a union joint with a lead tube similar to that used in the last experiment, having at its other end a strong

glass tube and steel tap. The bore through the joint was not less than that of the tube itself. The fulminate used was procured from the Roburite Explosives Company, in the form of detonators containing one gram each. After each explosion the bomb was immediately detached, and the end of the leaden tube stopped by a cork till its contents could be examined. In no case was there any flame in the glass tube at the other end, and on testing the contents of the tube it was found that the gas was never decomposed down the tube for more than about 15 cms. The acetylene in the bomb itself was decomposed, and the sides of the bomb were covered with a deposit of fine carbon.

A second series of experiments was then made, in which carbon bisulphide vapour was used instead of acetylene. This gave a different result. On attaching to the bomb described a strong glass tube 1¼ metres long, instead of the lead one, and filling the whole, by exhaustion, with vapour of CS_2, one of the same detonators produced complete decomposition of the gas, and a deposit of carbon on the whole of the inner surface of the glass. A repetition of the experiment gave a similar result. An attempt was then made to measure the rate of transmission of this explosion. The passage of the flame down the tube was timed by making it break in turn two silver "bridges" stretched across the tube, each bridge being connected with a magneto-electric style tracing a mark on a moving plate. In order to fire the fulminate at a given moment, the detonator was fastened by a caoutchouc ring in the end of a firing tube filled with electrolytic gas. This firing tube was screwed into the bomb, so that the detonator on one side was in contact with the electrolytic mixture, and on the other with the carbon bisulphide vapour in the bomb. The electrolytic gas was fired by the moving plate of the chronograph, and the explosion was transmitted to the fulminate, and so to the carbon bisulphide. The bomb, with the detonator in position, was connected with a long glass tube, having a silver bridge about one metre from the bomb, and a delicate arrangement, capable of being adjusted to be broken by a shock of greater or less violence at the other. The other end of the tube was closed by a tap, and the distance between the breaks was five metres. On repeating the experiment with this apparatus the decomposition was in no case propagated more than about 2·5 metres, the density of the

deposit decreasing with increasing distance from the bomb. On repeating the experiment with a lead tube coiled up in a water bath at 100°, the second bridge circuit was unbroken. The decomposition in the bomb itself is extremely violent, and a flash of intense yellow colour can be seen in the glass tube as far as the explosion proceeds.

It appears, therefore, from these experiments, that the decomposition by shock of acetylene and carbon bisulphide is not propagated like the explosion wave at a constant velocity as far as the gas extends, but that the decomposition set up by the fulminate dies out at a distance from the detonator, depending on the nature of the gas and, probably, also on the intensity of the initial shock and the cooling power of the walls.